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Formation of Triphenylpararosaniline Hydrochloride from Diphenylamine and Chloralammonia

By

Riki Horiuchi

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About 14 years ago M. Kuhara obtained a blue-coloured substance by heating diphenylamine and chloralammonia in a vacuum, and S. Idesaki[1] working under his direction confirmed experimentally that the blue compound is triphenylpararosaniline hydrochloride. The question of the mechanism of the formation having been left hitherto unsolved the author took up the problem and investigated how the reaction progresses.

I. Preparation of the blue compound and its properties

The blue compound was prepared according to Idesaki's description as follows: Diphenylamine and chloralammonia were mixed together in a molecular proportion and heated on a water bath for about one hour. By this treatment ammonia was evolved, but the diphenylamine was observed to remain practically unchanged. The mixture was then heated with direct fire at 130° C under a reduced or ordinary pressure, when it melted and then boiled. On continuing the boiling a sudden change of colour from green to blue took place and at the same time hydrogen chloride gas was evolved. The dark-coloured mass obtained on cooling was washed first with hot benzene

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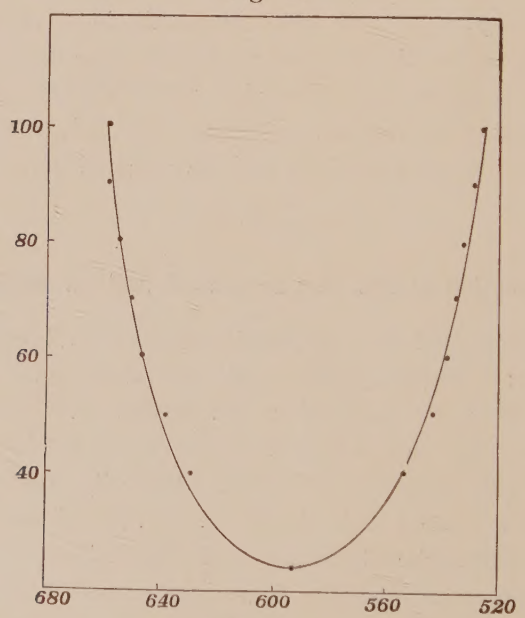
[1] Work not published.

and then with ether to remove the diphenylamine left unchanged, and treated with hot alcohol in which the blue compound readily dissolved. A concentrated hydrochloric acid was added to the alcoholic extract and the mixture left to stand for several hours, and later the blue precipitates formed were filtered. This process of precipitation was repeated several times, and finally the precipitates were washed with chloroform and recrystallized from alcohol or from aniline on addition of ether.

The substance thus purified was obtained as a crystalline powder with golden lustre as stated by Baeyer and Villiger,[1] and the brilliant blue colour of its alcoholic solution was seen to turn to reddish brown on addition of alcoholic sodium hydroxide, which shows that the corresponding free base, triphenylpararosaniline was thus formed. All its properties were found to agree exactly with those of triphenylpararosaniline hydrochloride. The absorption spectrum of its alcoholic solution showed only one absorption band whose maximum lies nearly at 593 $\mu\mu$, as may be seen in the following figure:

Fig. 1.



This fact agrees fairly well with the observation of Formánek.[2]

1 Ber. D. Chem. Ges., 37, 2872 (1904).

2 Formánek: Untersuchung und Nachweis org. Farbstoffe auf spectroscop. Wege.

II. Mechanism of the Reaction

In the preparation of the blue compound above described the previous heating of the mixture on a water bath is necessary, otherwise the yield becomes so poor that it can hardly be separated. If however chloralammonia heated once on a water bath be used, we can apply direct fire at once without the fear of lessening the yield. From this fact it is clearly to be seen that what takes part in the formation of the blue compound is not chloralammonia itself, but its decomposition products.

Now chloralammonia is known to undergo decomposition at 100° and to give the following substances as decomposition products :[1]

Chloroform.
Formamide.
Chloralimide.
Isochloralimide
Chloraldiformamide.

It is therefore to be decided which of these substances interacts with diphenylamine and produces the diphenylamine blue.

Looking at the general modes of formation of the dyestuffs belonging to the triphenylmethane series, we perceive that the carbon in the CHO group often becomes the central carbon atom of the dyestuffs thus :

$$C\begin{cases} C_6H_4NH_2 \\ H \\ O \end{cases} + 2C_6H_5NH_2 + O = HO-C\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4NH_2 \end{cases} + H_2O,$$

$$C\begin{cases} C_6H_5 \\ H \\ O \end{cases} + 2C_6H_5N(CH_3)_2 = H-C\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} + H_2O$$

$$H-C\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \end{cases} + O + HCl = C\begin{cases} C_6H_5 \\ C_6H_4N(CH_3)_2 \\ C_6H_4=N(CH_3)_2Cl \end{cases} + H_2O$$

But it is to be noted that all these reactions are only brought about

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1 Personne : Lieb. Ann., 157, 114 (1871), Béhal et Choay : Ann. chimi. phys. [6] 26, 5 (1892); 27, 319 (1892).

by aid of some oxidizing agent, without which the leucocompound first formed can not be further transformed into the coloured compound.[1]

Since there is no oxidising agent among the decomposition products of chloralammonia it seems impossible to regard the carbon in the aldehyde group as the source of the central carbon atom of the diphenylamine blue in this experiment. If this be admitted there is only one alternative, that is the central carbon in the diphenylamine blue can only be regarded as originating from the carbon in the trichloromethyl radical.

As to the reactions between the compounds containing the CCl_3 group and the aromatic amines not a few are mentioned in chemical literature. Girard and de Laire prepared diphenylamine blue from diphenylamine and perchloroethane, Döbner[2] obtained malachite green from dimethylaniline and benzotrichloride, and Hofmann prepared magenta by treating aniline with carbon tetrachloride. Some of these reactions take place only in the presence of a catalyser, but in no case is an oxidizing agent needed.

To confirm the above contention experimentally the behaviour of diphenylamine toward the compounds containing the aldehyde group on the one hand and toward those having the CCl_3 group on the other, was investigated. As the substance containing the aldehyde group, formic acid, acetaldehyde, formamide, formylphenylhydrazine and formanilide were selected, and each was heated with diphenylamine. All these experiments gave no satisfactory result the blue compound was obtained in not one instance. Formaldehyde[3] is known to act upon diphenylamine and to produce diphenylamine blue. But even with this some oxidising agent is needed, without which the reaction never progresses so as to produce diphenylamine blue. Next to know the behaviour of compounds containing the CCl_3 group carbon tetrachloride, chloroform, chloral, trichloracetic acid, chloralimide, isochloralimide, and chloraldiformamide were taken, and their action toward diphenylamine was studied. In this case diphenylamine blue was always produced, the only exception having been the action of chloroform which ended in the formation of the leucocompound.

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1 Hofmann: Lieb. Ann., 132, 296 (1864), O. Fischer: Ber. D. Chem. Ges. 10, 1625 (1877).

2 Ber. D. Chem. Ges., 11, 1238 (1878).

3 Farbw. Meister, Lucius and Brüning: Chem. Centralb., 1893, I, 1103.

a. Carbontetrachloride and Diphenylamine

A mixture of carbon tetrachloride and diphenylamine, with some zinc chloride added, was heated at 130° when the formation of the blue compound quickly took place, followed by the evolution of hydrogen chloride. Some reddish-coloured compound was produced as the by-product from which diphenylamine blue could easily be separated, as the former is more soluble in alcohol. The reaction may be represented as follows :

$$Cl-C\begin{matrix}Cl\\Cl\\Cl\end{matrix}+3C_6H_5NHC_6H_5=Cl-C\begin{matrix}C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\end{matrix}+3HCl$$

$$Cl-C(C_6H_4NHC_6H_5)_3=C\begin{matrix}C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\\C_6H_4:NC_6H_5HCl\end{matrix}$$

b. Chloroform and Diphenylamine

Diphenylamine was heated with chloroform in the presence of zinc chloride. No colour change took place. The addition of an oxidising agent such as arsenic acid, however, quickly brought about the change. It is therefore very clear that the leuco-compound of diphenylamine blue was formed by their interaction thus :

$$H-C\begin{matrix}Cl\\Cl\\Cl\end{matrix}+3C_6H_5NHC_6H_5=HC\begin{matrix}C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\end{matrix}+3HCl$$

c. Chloral and Diphenylamine

When chloral was heated with diphenylamine the formation of the blue was accompanied with the evolution of gas which was proved to consist of a mixture of hydrogen chloride and formaldehyde. Judging from this fact the representation of the reaction by the following scheme seems probable.

$$H-\underset{O}{C}-C\begin{matrix}Cl\\Cl\\Cl\end{matrix}+3C_6H_5NHC_6H_5=H-\underset{O}{C}(C_6H_4NHC_6H_5)_3+3HCl$$

$$H-\underset{O}{C}-C(C_6H_4NHC_6H_5)_3+HCl=C\begin{matrix}C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5+HCHO\\C_6H_4:NC_6H_5HCl\end{matrix}$$

d. Trichloracetic acid and Diphenylamine

The reaction between trichloracetic acid and diphenylamine took place easily and diphenylamine blue was produced. In the gas evolved in the reaction the presence of formic acid was confirmed.

$$HOOC-CCl_3+3C_6H_5NHC_6H_5=HOOC-C(C_6H_4NHC_6H_5)_3+3HCl$$

$$HOOC-C(C_6H_4NHC_6H_5)_3+HCl=C\begin{cases}C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\\C_6H_4:NC_6H_5HCl\end{cases}+HCOOH$$

e. Chloralammonia and Diphenylamine

As was described before chloralammonia and diphenylamine react together at 130° to form triphenylpararosaniline hydrochloride, though the yield is very scant. The reaction may be represented as follows:

$$CCl_3CH(OH)NH_2+3C_6H_5NHC_6H_5=NH_2(OH)CH-C(C_6H_4NHC_6H_5)_3+3HCl$$

$$NH_2(OH)CH-C(C_6H_4NHC_6H_5)_3+HCl=C\begin{cases}(C_6H_4NHC_6H_5)_2\\C_6H_4:NC_6H_5HCl\end{cases}+HCHO+NH_3$$

In like manner chloralimide, isochloralimide and chloraldiformamide were all found to react with diphenylamine so as to produce diphenylamine blue as the reaction product.

III. Conclusion

1. When heated directly at 130° diphenylamine and chloralammonia produce only a small quantity of triphenylpararosaniline hydrochloride; if the mixture is heated at 100° for some time and then the temperature raised to 130° the yield of the dyestuff is greatly increased.

2. In order to seek for the cause of the reaction the interaction between diphenylamine and each of the decomposition products produced from chloralammonia at 100° was studied, and a generalization was attained as follows: that the compounds which take part in the formation of diphenylamine blue are those containing the CCl_3 group but not the CHO group.

3. To explain the mechanism of the reaction the author put forward an assumption that the chlorine atoms in the CCl_3 group are replaced by the phenyl group, and the substance thus produced further changes in the dyestuff by the action of hydrogen chlorine as is shown by the following equation:

$$R-C\begin{cases}Cl\\Cl\\Cl\end{cases}+3H\,C_6H_4NHC_6H_5=R-C\begin{cases}C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\\C_6H_4NHC_6H_5\end{cases}+3HCl$$

$$R-C\begin{cases}(C_6H_4NHC_6H_5)_2\\C_6H_4NH\,C_6H_5\end{cases}+HCl=C\begin{cases}(C_6H_4NHC_6H_5)_2\\C_6H_4=NC_6H_5\cdot HCl\end{cases}+RH$$

The author wishes to express his sincere thanks to the late Prof. M. Kuhara under whose direction this work was carried out.

On the Velocity of Formation of Barium Peroxide

By

Nobuji Sasaki

(Received March 7, 1921)

Introduction

The formation of barium peroxide from barium oxide and oxygen at high temperatures is an example of a sort of heterogeneous gas reactions, a sort not so common as those which have hitherto been investigated. For in this case, besides the solid reactant, the product of reaction is also a solid substance. During the reaction, therefore, the solid reactant is always changing its state both physically and chemically, being covered by a growing layer of the more or less impure reaction product. It may be an interesting problem, however, to investigate the velocity of reaction of such a complicated nature from the stand point of chemical kinetics.

As to the earlier investigations of such a heterogeneous gas reaction, there is only one so far as I could discover. This is the decomposition of silver oxide investigated by G. N. Lewis.[1] He explains the accelerated velocity of decomposition by the autocatalytic action of the liberated silver particles and a mathematical expression of the reaction velocity is deduced by assuming that the decomposition is a *homogeneous* autocatalysed reaction, the velocity being proportional to the amount of silver liberated. The theoretical and the experimental curves are in good accordance.

1 Zeitsch. f. physik. Chem., Vol. 52. p. 310, 1905.

Experimental Part

Method of investigation.—In the present experiment, there is a considerable difference of temperature between the inside and the outside of the reaction chamber, and the pressure within it also differs more or less from that of the atmosphere. Moreover, the condition of the reacting substance is comparatively rapidly affected by the change of temperature and of pressure. In such a case, the attempt to study the velocity of reaction by analysing chemically a part of the reacting substance which is successively taken out from the reaction chamber, may always be accompanied by some unavoidable errors. Because, in consequence of the change of temperature and of pressure which the sample suffers after its withdrawal, its chemical composition may have changed considerably before it is subjected to analysis. But even in the absence of this facility of change of composition, such a method of investigation is unsuitable for the study of the velocity of heterogeneous reactions in general. The reasons are as follows:

The solid substance to be taken at first for one experiment must be of such amount, that it may be sufficient for successive withdrawals of samples for analysis. Every point of the solid mass, therefore, can not be under the same conditions: the uniform temperature of the solid may be attained by limiting its extension, but on behalf of this the uniform contact of the solid with the reacting gas must no more be expected. The latter uniformity may be achieved by extending the solid, but in turn, the former uniformity must be sacrificed. Thus, each point of the reacting solid has its own conditions of reaction and consequently proceeds to react at its own velocity. It is, therefore, evident that a part of such a reacting mass, when analysed, gives neither a stage of a single reaction under certain conditions, nor a stage of the resultant of all the reactions occurring in the whole solid mass. If it could give even the latter, it might be possible, by some mathematical means, to take into account the influences due to the non-uniformities of temperature or of other conditions as will be done in the following theoretical part. A portion of the solid mass taken out in practice is, generally, not the summation of a certain fraction of every part of the solid, where the reaction proceeds at it own velocity. From this it is obvious that such a portion taken out can not give a stage of the resultant of all the reactions taking place

throughout the solid. A mathematical explanation will show more clearly what is meant.

Let the mass of a portion of the solid mass under certain conditions A be denoted by M_A and that of the portion under some other conditions B by M_B, and so on. Then a stage of the reaction of the solid mass taken as a whole may be given by analysing

$$M_A + M_B + \ldots\ldots$$

or a certain fraction of this

$$nM_A + nM_B + \ldots\ldots$$

But the constitution of the portion taken out in practice may be represented by

$$n'M_A + n''M_B + \ldots\ldots$$

where n's are generally unequal positive fractions; some may even be zero.

Comparing the latter two expressions, it is quite clear that such a portion of the solid cannot give a true state of the solid mass, taken as a whole, at the time of withdrawal.

Such an inconvenience may be avoided (1) by pulverizing the solid substance and continually stirring the powder all the while the reaction proceeds, but the contrivances may become too complex; or (2) by preparing a number of blocks of the solid substance all identical in form and in other qualities and taking them out one by one successively for analysis; but such identical blocks may be difficult to prepare.

After all there is nothing better than to work with $M_A + M_B + \ldots\ldots$ itself, that is to say, to use the sample all at once.

In this case, however, the original sample must be used repeatedly without suffering any change at all. This can only be attained by some mechanical contrivances.

At first we remember the well-known manometric method which has been often used with advantage. But this method must not be employed in the present experiment, where the air is to be used instead of pure oxygen, partly because of experimental convenience and partly because of considering the practical industry.

The reason is thus: unlike the reaction in the formation of sulphur trioxide by catalysis or in the formation of nickel carbonyl from the metal, the reaction of the present case occurs not only on the surface of the solid phase but also it even penetrates into the very centre of the solid. Consequently it follows that the solid phase of

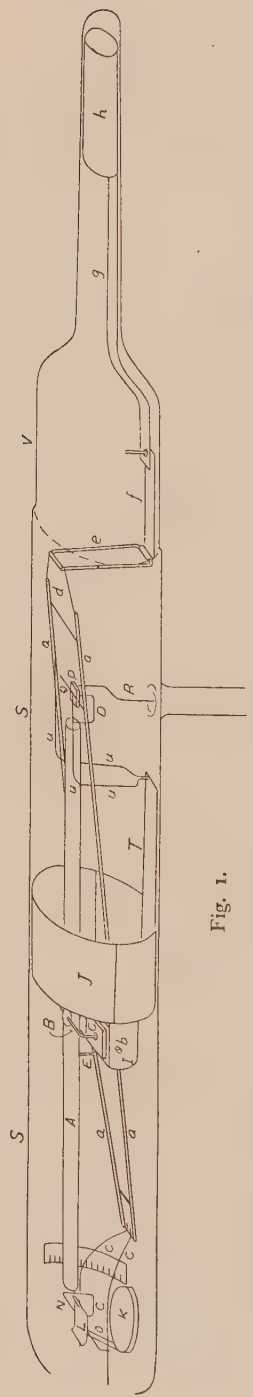


Fig. 1.

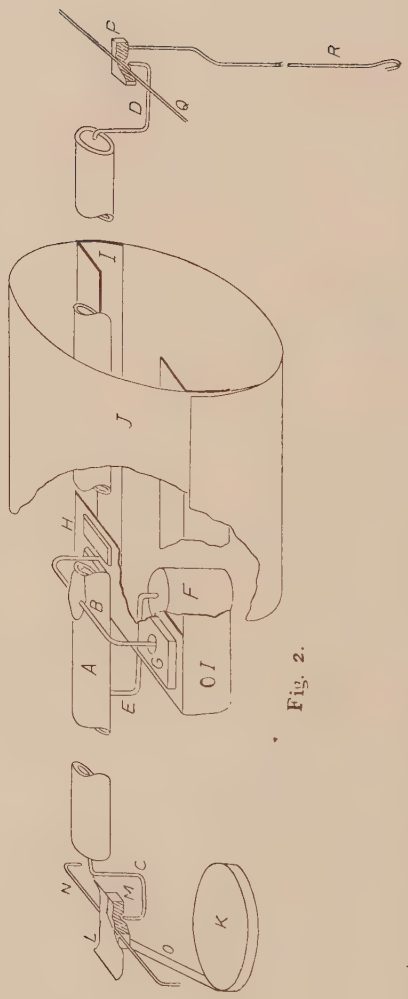


Fig. 2.

relatively small extent absorbs a relatively large amount of gas, thus the so called "schädlicher Raum" becoming noticeable. Moreover, the change of pressure of the gas phase must be taken into account in the mathematical treatment of the experimental results. But the increase of a variable may greatly complicate the treatment, although, as a matter of course, the manometric method exists thanks to this pressure change itself.

At any rate, the direct measurement of the increase of weight of the reacting solid is the most desirable, provided that a balance suitable for this purpose can be resorted to.

The balance to be described below was devised and constructed by myself and found to be very convenient for the weighing of a body at any temperature and pressure.

Referring to the accompanying diagrams, Figs.1 and 2, the construction of the balance will be fully described.

The balance beam.—*A* in Fig.1 is a piece of glass tube 4 mm. in diameter and 21 cm. in length and serves as a balance beam. Inside this tube, a ribbon of section paper of the same length is inserted and pasted to the lower side of the inner wall. On this ribbon a small piece of nickel wire of *ca.* 14 mg. weight is placed, which can be shifted freely along the tube by means of a bar magnet. This piece of nickel wire serves as a rider of the ordinary balance, the displacement of which can be measured by the ribbon of section paper. A U-shaped piece of steel wire *B* is firmly fixed with sealing wax to the middle point of the beam in crossed position, both its ends being sharply pointed. These pointed ends, as a substitute for the knife edge of the ordinary balance, keep their positions by *G* and *H*. *G* is a piece of brass plate with a conical hole on the upper surface. *H* is a narrow groove formed by two pieces of brass plate in parallel position. At a point *E* under the beam, a short distance from the middle point, one end of a piece of copper wire is fixed with sealing wax, the other end carrying a movable brass weight *F*. This weight is just below the steel wire *B* and is fixed to the copper wire with a screw not shown in the figure. By moving this weight *F* up or down, the stability of the beam, or its centre of gravity may easily be adjusted. At each end of the beam a brass needle of hook shape, *C* and *D*, is fixed with sealing wax. Upon the sharp ends of these needles the balance pans are to be hung.

The pans and the others.—*K* is a lead disc plated with nickel and

connected to the upper part by a piece of brass plate *O*. This heavy lead disc serves to impart the pan its stability. *M* is a piece of thick brass plate with a conical hole on its lower surface, which is the seat of the sharp end of the needle *C*. A piece of nickel wire *N* and a small brass pan *L* are fixed on *M*.

At the right end of the beam, there is a piece of brass plate *P*, similar to *M*, which rests upon the sharp end of the needle *D*. To *P* are fixed two pieces of nickel wire *Q* and *R*, *Q* being horizontal and *R* being vertical with a hook at its lower end.

The three parts so far described, that is, the beam and the two pans, constitute a movable system which is mounted on the fixed holders *I* and *I* by *G* and *H*, and is allowed to oscillate freely in a vertical plane. The holders *I* and *I* are fixed to a hollow cylinder *J*, which is made by doubly winding a sheet of thin brass plate. Since the outer end of the sheet is left free to be able to act as a spring, *J* can be firmly fixed inside the glass tube *S*. To the lower part of *J* is soldered a piece of brass plate *P*, from the free end of which two pieces of copper wire *u* and *u* project vertically.

Besides the moving system above mentioned, there is another, the main part of which is a lever consisting of two stout copper wires *a* and *a*. It is supported by two pivots *b* and *b* embedded in *I* and *I*. From the left end of the lever project two pieces of copper wire *c* and *c*, reaching beneath the nickel wire *N*. The right half of the lever ends at *d*, the copper frame *a* and *a* running outside the wires *u* and *u*. The lever-end *d* and the soft iron bar *h* at the extreme end of the balance case are connected movably by *e* and *f*.

The right part of the balance case is a glass tube *V* which is inserted inside the glass tube *S* and sealed air-tight with sealing wax. To the tube *S*, just below the right end of the beam, a side tube is attached, through which passes a wire connecting the hook of *R* and the sample suspended in the furnace. A piece of scaled paper is pasted to the wall of the balance case just opposite the left end of the beam.

The left end of the balance case is connected with two glass tubes in which the balance weights are to be arranged.

Balance weights.—The larger weights were made by cutting a small soft iron bar into short pieces of proper length and the pieces nickelplated. The smaller weights were made by coiling up pieces of nickel wire of the proper length. The smallest weight weighs

ca. 20 mg., and the next one *ca.* 40 mg. Thus increasing each successive piece by *ca.* 20 mg., the largest and heaviest weighs *ca.* 500 mg. These weights were exactly calibrated.

So far the description of the construction of the balance. In the following paragraphs will be explained how the balance is used.

Arrangement of the weights.—At the beginning of an experiment, in one of the tubes attached to the balance case, the weights are arranged in the order of their magnitude, at proper distances from each other, the smaller ones being placed nearer the balance. As the solid sample under weighing increases its weight in the course of the reaction, the weight on the pan *L* must successively be replaced by a larger one. The weights thus used are carried into the other tube one after the other, where they find themselves arranged in the order of their magnitude, the larger ones being nearer the balance. Since, in this manner, the weights are always arranged regularly and never come into confusion, they may be used as often as may be desired. As the weights can only be carried about by a magnet, this regular arrangement is of great importance, for, otherwise, it is a matter of difficulty to select one from the weights lying irregularly side by side.

Around the tube *U*, in which the iron bar *h* is placed, a coil is loosely fitted which can produce a strong magnetic field in its bore, when the electric circuit is closed. According as the iron bar is shifted from right to left or from left to right by means of this coil, the left end of the lever will move up or down.

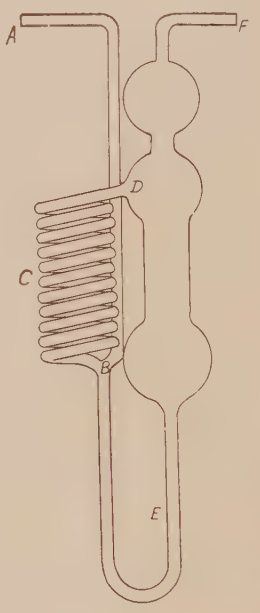
The weights are carried about by a horse-hoof electromagnet whose two ends are brought very near to each other. With such a magnet it is easy to pick up one of the weights, for the magnetic field is confined very near the poles; otherwise, other weights may be apt to be attracted all at once. But with precautions a bar magnet may also be used which has its own advantage.

To bring a weight upon or to take it off from the pan L.—The nickel wire *Q* at the right end of the beam is turned by a bar magnet, so that it may not touch the wires *u* and *u* during its vertical motion. Then the nickel wire *N* of the left pan is turned to crossed position with the wires *c* and *c*. The coil, with its circuit closed, is now shifted from right to left, so that the wires *c* and *c* lift up the pan by the wire *N*. When the pan has reached a proper position, the circuit is cut off. Now by a horse-hoof magnet the weight next to the balance is

carried to just above the pan and let fall upon it by cutting off the current. Then the iron bar *h* is carried back to its original position. In order to remove the weight from the pan, it is only necessary to conduct the above process exactly in the reversed order.

To know the total weight of P, Q, R and the connecting wire with the sample at its end, all of which are hung on the needle D.— By repeating the process above mentioned, such a weight may be chosen as is just short of balancing the beam. Now by means of the bar magnet the wire *Q* is lifted up and turned horizontally so that *Q* may cross the wires *u* and *u* The iron bar *h* is then displaced from right to left, the pan *L* being raised accordingly. In the mean time, the needle *D* will become free from the load of the system, *Q*, *R*, etc., the latter being left to rest upon the wires *u* and *u*. Then the pan *L* also comes off from the needle *C* to be supported by the wires *c* and *c*. Thus the beam can now oscillate freely by itself. By means of the bar magnet, the rider is brought to such a position that the left end of the beam may oscillate about the zero point of the scale as the centre. The position of the rider is read. The next time, the iron bar is shifted to the right and the beam is loaded with the pans. The rider is again moved to such a position that the left end of the beam may oscillate about the zero point as the centre. The position of the rider is read. Now the weight of the pan together with a weight on it, the beam ratio and the correction of weight due to the displacement of the rider (4·7 divisions = 1 mg.) being all known constants, the total weight of the bodies hanging on the needle *D* may be calculated from the preceding two readings of the rider.

Fig. 3.



In the following pages, the whole apparatus used in the experiment will be described.

Two new types of gas washer.—The accompanying figure, Fig. 3, shows one of the newly devised gas washers. The whole apparatus is made of glass. Gas enters at *A* and leaves at *F*. *C* is a worm tube, the upper end *D* of which is sealed to the wall of a wide tube. The

washing liquid is contained in this wide tube. The lower end of the tube and that of the worm tube are connected by a tube *E*. The gas-inlet-tube opens at *B*. The gas that has entered at *A* is divided into small bubbles at *B* and these bubbles, intimately in contact with the washing liquid, rise up along the worm tube, and arriving at *D*, separate from the liquid and escape by *F*. As thus the liquid is always circulating in the apparatus, all its portions come equally in contact with the gas.

There has been used a type of gas washer with a worm tube devised by Gahl.[1]

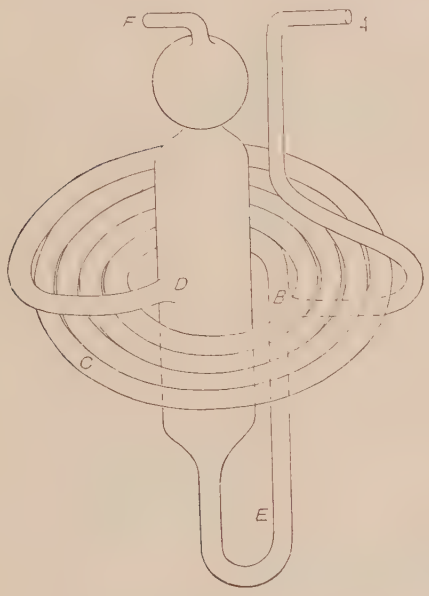


Fig. 4.

With this washer, however, when the velocity of the gas flow is more or less increased, the gas is apt to bubble off outside the worm tube. Moreover, the gas bubble ascends the worm tube with a velocity depending only on its buoyancy. For this reason, the time of contact of the gas with the liquid is short, even when the flow of gas is slow. But with my new washer, the time of contact may be prolonged as much as is desired by making slower the flow of gas.

In order that the gas may pass through the worm tube, it must overcome a hydrostatic pressure corresponding to the height of the worm. This inconvenience is common to both types old and new. But this may be avoided in the following way:—

1. Reducing the height of the worm tube by increasing the diameter of the coiling.

2. Using a spiral tube instead of the worm as in Fig. 4. With this kind of convoluted tube, the hydrostatic pressure to be overcome becomes almost zero.

Obviously, such improvements are not to be applied to the old type.

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1 Kurt Arndt, Handbuch der physikalisch-chemischen Technik, p. 235.

Gas washers of these new types may easily be constructed in the laboratory, for they require no difficult manipulations, such as grinding.

The accompanying figure, Fig. 5, shows the arrangement of the apparatus used in the experiment.

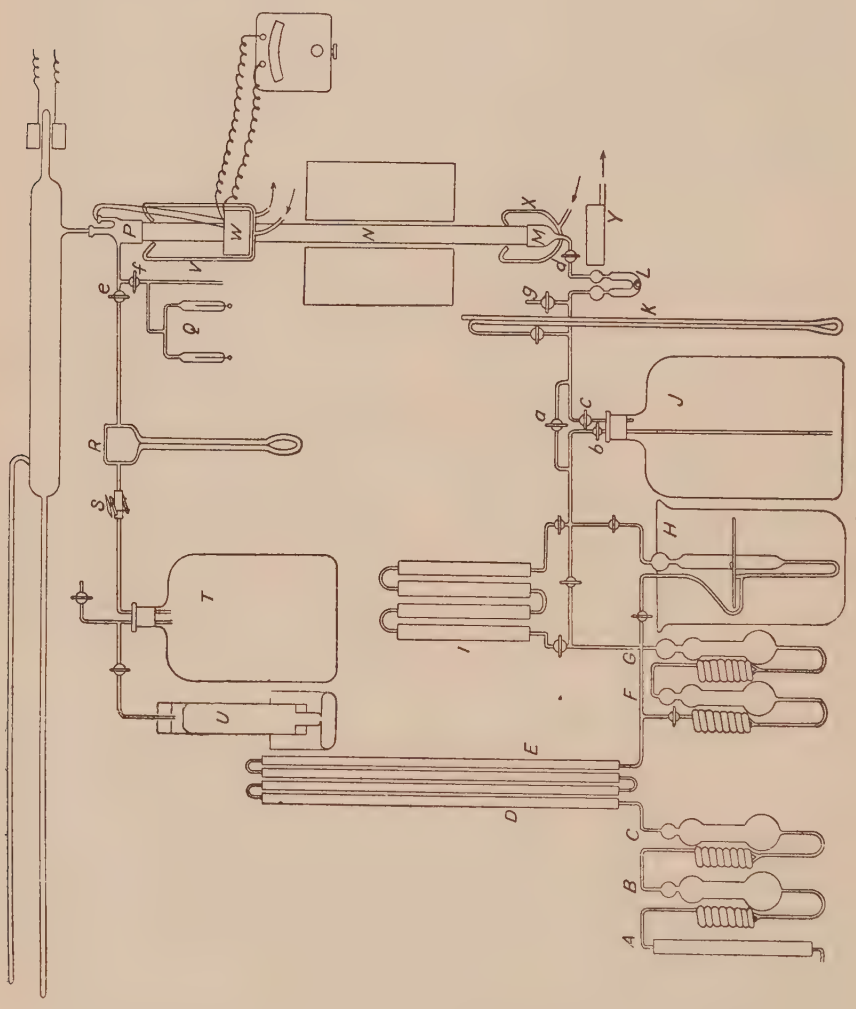

Fig. 5.

The air enters at the lower end of the tube *A* which contains cotton-wool so that dust and micro-organisms may be filtered off from the air.

Two gas washers *B* and *C* contain a potassium permanganate solution which serves to oxidise the organic gases contained in the

air and convert them into water and carbon dioxide. The gas saturated with water vapour in these washers is dried in the tube *D* which contains granulated fused calcium chloride.

Three tubes *E* each contain soda lime granules in order to absorb carbon dioxide from the air. The gas leaving the last tube of *E* may reach the gas holder *J* by any one of the three ways. The first is to pass through the gas washers *F* and *G* which are filled with concentrated sulphuric acid of known strength. The air may here acquire a certain water vapour pressure corresponding to the concentration of the acid. The second is to pass through *F*, *G* and the tubes *I*. These tubes are filled up with glass wool on which phosphorus pentoxide powder has been thickly sprinkled. The third is to pass through the washer *H* only, which is filled with carbon dioxide free water. *H* is immersed in a flask containing water of known temperature. The air may here acquire a certain water vapour pressure corresponding to the temperature of the water. The air which has passed any one of these three ways may either flow into the gas holder *J* by the cock *b* or may pass on further through the cock *a*. The gas holder is used at the beginning of an experiment in order to fill up the evacuated furnace tube with proper rapidity. *K* is a manometer; *g* is a side tube connected with a suction pump. *L* is a U-tube at the bottom of which a drop of mercury is placed. The vibration of this drop may roughly indicate the velocity of the flow of gas. This is used to prevent the flow of gas from becoming too violent when the evacuated tube is first filled up with the air in the gas holder *J*. Now the air enters at the lower end of the furnace tube and, ascending upward, reacts with the sample which lies in its way. The remaining gas leaves the tube at the upper end and arrives at *R*. *R* is a differential velocity indicator. *S* is a screw pinch cock which is used to regulate the velocity of gas flow. The air enters finally into the bottle *P*. The pressure inside the bottle is maintained constant by means of a suction pump and a pressure regulator *U*. The lower end of the tube *U* terminates in a small hole through which mercury enters to ascend to a certain height. This height of the mercury column corresponds to the difference of the pressures inside and outside the bottle *P*. As soon as the pressure inside *P* is reduced any more than necessary, the outside air bubbles into the tube to compensate for the excess. The exit-tube for the gas from the furnace has a side tube with a cock *f*. This side tube is connected to a Gaede's rotary mercury

pump and a vacuum discharge tube *Q* provided with an induction coil.

The furnace employed is an electric resistance furnace of 20 cm. length with platinum ribbon. The porcelain tube inserted in the furnace is 60 cm. in length, the inner diameter being 2 cm. Each end is closed with a glass cap, *M* and *P*. Of the three tubes projecting from *P*, the middle one is connected with the side tube of the balance case, the left one for the exit of gas and the right one for the insertion of a Pt-PtRh thermocouple. The temperature of the furnace is measured by the thermocouple and a Siemens-Halske's millivoltmeter. The cold junctions are placed in the water receiver *W*. The upper and lower parts of the furnace tube are cooled by means of the apparatus *V*, *W* and *X*, *Y*, using cold water.

Method of experiment.—A piece of platinum wire gauze containing barium peroxide tabloids is fastened to one end of a fine platinum wire, the other end of which is hung to the hook of the nickel wire *R* in the balance case. The length of the platinum wire is so chosen that the sample may just reach the middle part of the furnace. The cap *M* is then attached to the lower end of the furnace tube, the cap *P* having been fixed beforehand. The side tube of the balance case and the middle tube of the cap *P* are connected with sealing wax.

Closing the cock *a* and opening the cocks *b* and *c* of the gas holder, the cock *g* is opened which communicates with the suction pump in action. Washed CO_2-free air now streams into the gas holder through the cock *b* and flows out through the cock *c*. When the content of the gas holder is completely replaced by the CO_2-free air, the cocks *b*, *c* and *g* are closed. Now by means of a mercury pump, air is drawn out through the cock *f* from the balance case and the furnace tube, with the cocks *d* and *e* closed. When sufficiently evacuated, *f* is closed. The heating of the furnace is then commenced. When the temperature has risen sufficiently high, *f* is opened and the dissociated oxygen is drawn out by the vacuum pump. Now the vacuum discharge tube *Q* plays its roll. The glow in the tube produced by the electric discharge begins at about 40 mm. Hg. At first it is a streamer but when the vacuum attains as high as 0·03 mm. Hg, the wall of the tube acquires a greenish yellow fluorescence. Between these two extremities, there are various stages of glowing, changing sensibly with the pressure. By this appearance of discharge glow, therefore, the course of decomposition of barium

peroxide may be followed. The exhaustion of oxygen is continued until the green fluorescence appears, which, on stopping evacuation, remains unchanged showing that no further evolution of oxygen is taking place. Now the electric current of the furnace is regulated so that the furnace may be kept at a certain desired temperature. The weight of the sample is then measured. The suction pump is now set in action, by which the pressure inside the bottle *P* is kept constant. The cock *c* of the gas holder is opened. Watching the motion of the mercury drop at *L*, the cock *d* is then gradually opened, through which the air in the gas holder begins to flow into the furnace tube with a proper velocity. In about half a minute this flow will come to an end. This moment is taken as the starting point of the reaction. Now closing *c* at once, the cock *a* is gradually opened. Air is then washed afresh and flows into the furnace tube directly, which is all filled up in about half a minute more. At this moment, the cock *e* is opened. Air will now begin to flow through the whole apparatus with a constant velocity of *ca.* 120 bubbles per minute. From this time on the increase of weight of the sample is measured now and then by displacing the rider and replacing the weight.

The sample is weighed at first in the vacuum and the subsequent weighings are carried out in the air of almost one atmosphere. But the influence of the buoyancy of the air is so small that it may be neglected without committing any significant error. The ascending air in the furnace tube may collide with the sample, apparently reducing its weight. But this collision does not produce any noticeable effect, probably because the velocity of flow is very small in this wide tube.

Preparation of sample.—The ordinary preparative method of obtaining barium oxide by decomposing nitrate by heat is inconvenient and not to be employed in the present investigation. For, besides admixture of impurities during the fusion, the product will rapidly absorb moisture and carbon dioxide during its pulverisation and further manipulations. In order to avoid such inconveniences, Merk's sample of barium peroxide octahydrate, pur., was taken. The peroxide was dehydrated completely in a vacuum desiccator with phosphorus pentoxide. The powder thus dehydrated was compressed into small tabloids of identic size. About a dozen of these were wrapped in a piece of platinum wire gauze and placed inside the furnace to be suspended to the nickel wire *R* by means of a piece of fine platinum wire. The oxide is then prepared by decomposing this peroxide by heat and drawing

out the oxygen thus formed as described in the preceding section. Heating was continued for several hours, the temperature being kept at about 900°. During this time, evacuation was carried out from time to time until no further decomposition could take place.

The weight of the peroxide taken was 1·260 gr. and the final loss of weight was 0·076 gr. Therefore, the oxide thus obtained contained yet 35% peroxide.

With this sample, the rate of oxidation at a certain temperature is measured. Then by decomposing the reaction product once more, the original state of the sample may be restored. With this one sample, therefore, measurement may be repeated as often as we please.

On the basis of the experimental data as given in the last part of this paper, graphical representations are tried on the following page, Fig. 6.

Theoretical Part

As shown in the graphical representations, Fig. 6, the curves are of very peculiar type. This peculiarity is, indeed, the most interesting point in the present investigation, for it indicates an extraordinary course of the reaction between barium oxide and oxygen.

We will now consider the mechanism by which barium oxide molecules in the solid begin to react with oxygen one after the other, and will, with various assumptions, deduce mathematical expressions which represent the course of the reaction quantitatively.

First of all, the problem must be examined : how does the reaction proceed when a solid substance reacts with a gaseous substance to form a solid reaction product which is, for its part, soluble in the solid reactant ?

In cases of heterogeneous reactions such as the formation of sulphur trioxide by catalysis, or the formation of nickel carbonyl from the metal, the reactions take place only on the surface of the solids. In the present case, however, the reaction occurs at first on the surface but soon after it penetrates into the interior of the solid. The simple ideas, therefore, which have been useful for the hitherto investigated heterogeneous reactions, have nothing to do with the theoretical treatment of the present problem.

In what follows it is attempted to obtain a mathematical solution by transforming the problem into that of heat conduction.

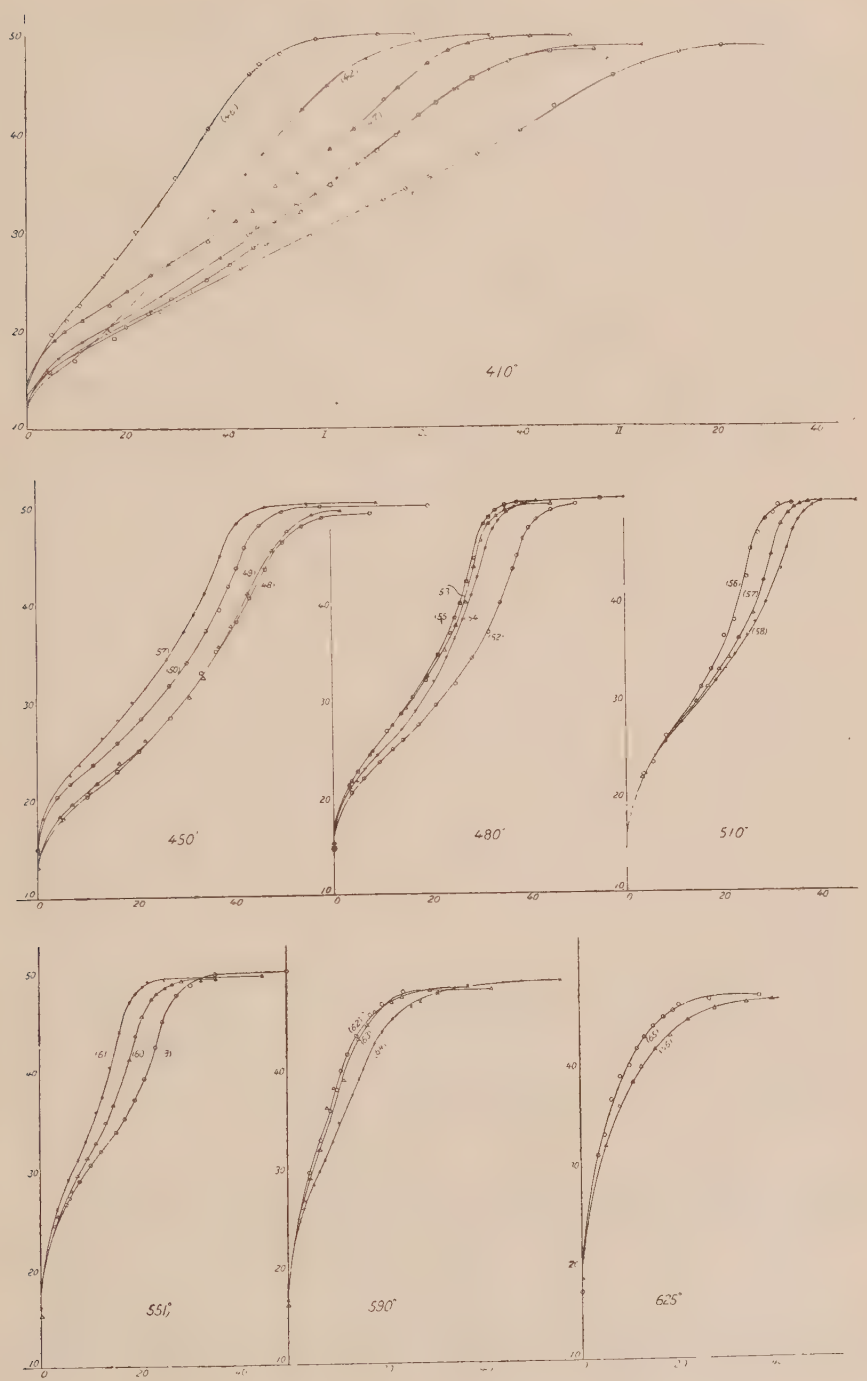

Fig. 6.

According to the investigation of J. H. Hildebrand[1], barium oxide and peroxide are soluble in each other to some extent. But the limits of their mutual solubilities at a certain temperature vary over a wide range, being considerably affected by the state of the samples employed. In the following treatment, a limitless solubility is assumed for simplicity's sake.

Some analogies between the phenomenon of heat conduction and that of barium peroxide formation must now be considered.

Let "heat" be a hypothetical substance, then a warm body is a solid solution of the conducting material and the heat it contains. There is no limit of solubility. Hence the heat may be compared with oxygen and the conducting material with barium oxide.

Whether barium oxide reacts with oxygen in a molecular state or in an atomic state, is not at present in question. At any rate, the pressure of active oxygen in the gaseous phase, v_o, which is kept constant throughout the reaction, must be the same as the decomposition pressure of a solid solution of barium oxide and peroxide which has attained the state of equilibrium in this atmosphere. Here the decomposition pressure of a solid phase means the partial pressure of active oxygen only, which is in equilibrium with the solid phase. In the case of heat conduction, the temperature of the medium, v_o, which is always kept constant, must be the same as that of a body which has attained the state of equilibrium in this medium. Hence the partial pressure of active oxygen of the gaseous phase, or the final decomposition pressure of the solid phase is a physical quantity comparable to the temperature of the medium in the case of heat conduction.

When the oxide reacts with oxygen, there results an oxide solid solution of the peroxide. A point of this solid solution has a certain decomposition pressure corresponding to its own peroxide content. For simplicity's sake this decomposition pressure is assumed to be proportional to the concentration of the peroxide. Then it follows that the decomposition pressure at a point of the solid solution is a physical quantity corresponding to the temperature at a point of a warm body. This proposition may be explained as follows:

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[1] J. Amer. chem. Soc., 1912, Vol. 34, 246-258. His measurements were carried out with those states of equilibrium attained in the course of the peroxide decomposition. Those equilibria to be attained in the course of the peroxide formation were not measured for the purpose of confirming the results.

The peroxide contained in the solid solution will migrate from the portion of higher to that of lower peroxide concentration. The velocity of this migration may be assumed to obey the fundamental law of heat conduction, that is, that the velocity is proportional to the concentration gradient taken along the path of migration. But the dissociation pressure being proportional to the peroxide concentration, the gradient of dissociation pressure is also proportional to the gradient of peroxide concentration. Hence the velocity of migration of the peroxide is proportional to the gradient of dissociation pressure.

So far as the result is concerned the migration of the peroxide is at once the transference of oxygen. But oxygen can, for its part, also migrate independently. The decomposition pressure of a solid solution of higher peroxide concentration being greater than that of a solid solution of lower peroxide concentration, oxygen will migrate away from the portion of higher to that of lower peroxide concentration, with a velocity also proportional to the gradient of dissociation pressure. Consequently the solid solution of lower dissociation pressure becomes richer in the peroxide.

These two sorts of migration may be regarded as the same thing as to their results as well as to their manners. Because, so far as their results are concerned, the migration of a peroxide molecule is nothing other than the separation of an oxygen atom from the peroxide molecule to recombine with the oxide molecule which the peroxide molecule was to replace. As to their manners of migration, the peroxide obeys the same law as oxygen does, that is, each velocity of migration is proportional to the gradient of dissociation pressure. Let the gradient be denoted by G. Then, the velocity of the migration of the peroxide is KG, where K is a proportionality constant ; and the velocity of the migration of oxygen is $K'G$, where K' has the same meaning as K. When these two migrations occur at the same time, the total migration velocity of oxygen is given by a single expression

$$(K+K')\ G, \text{ or simply } kG.$$

Hence the migration of the peroxide and that of oxygen may be regarded as the migration of one substance only.

By comparing such a fluidal motion of oxygen with the flow of heat in a conducting substance, it is now quite evident that the dissociation pressure at a point of an oxide solid solution has the same meaning as the temperature at a point of a conducting body.

By the propositions hitherto mentioned, the problem of the heterogeneous reaction has completely been transformed into the problem of heat conduction. But before applying the theory of heat conduction to the present case, it is necessary to have clear ideas about the meanings of the physical quantities such as heat capacity, thermal and thermometric conductivity, etc.

The heat capacity of a substance is the quantity of heat to be added to a unit mass of the substance in order to raise its temperature by unity. Heat corresponds to oxygen and temperature to dissociation pressure. Hence the physical quantity corresponding to the heat capacity is the quantity of oxygen to be added to "a unit mass" of the oxide solid solution in order to elevate its dissociation pressure by unity. Let this quantity be denoted by the symbol c. Remark: in this definition, the oxygen combined with the oxide is assumed to be weightless, otherwise, "the unit mass" has no meaning. See also the definition of "density" described on the next page.

The thermal conductivity of a substance is the quantity of heat which flows across a unit area of an isothermal surface in a unit of time, when the temperature gradient, taken along the outward drawn normal to the surface at that point, is unity. As the temperature gradient corresponds to the gradient of dissociation pressure, the corresponding physical quantity of the thermal conductivity is the quantity of oxygen, denoted by K, which flows across a unit area of a surface of equi-dissociation-pressure in a unit of time, when the gradient of dissociation pressure is unity—when peroxide molecules pass there, the quantity of oxygen carried by them must also be taken into account. If the gradient of dissociation pressure is $\frac{\partial v}{\partial n}$ instead of unity, the above quantity of oxygen is

$$-K\frac{\partial v}{\partial n},$$

where v: dissociation pressure,

$-\frac{\partial}{\partial n}$: differentiation in the direction of outward drawn normal to the equi-dissociation-pressure-surface, and the minus sign is necessary, for the amount of oxygen is counted positive when it flows in the positive sense of the normal.

The thermometric conductivity of a substance is defined by the relation

$$\varkappa = \frac{K}{c\rho},$$

where $\varkappa$: thermometric conductivity,
K: thermal conductivity,
c: heat capacity,
ρ: density of the substance.

If to the quantities K, c and ρ their corresponding meanings are ascribed respectively, $\varkappa$ may be regarded as a physical quantity which corresponds to the thermometric conductivity.

Here a word about the meaning of ρ. The temperature variation of the density of a solid substance is a very small one. In the theory of heat conduction, therefore, this influence of temperature is neglected. But in the present case, the density of an oxide solid solution increases considerably as it absorbs oxygen. In order to avoid such an inconvenience the density must be defined as a definite quantity that is proportional to the number of barium atoms contained in a unit volume of the sample. As in the case of heat conduction, it must also be assumed that the density thus defined is independent of the quantity of oxygen absorbed, that is, the distance of barium atoms from each other is not altered by absorbing oxygen.

Now the theory of heat conduction may directly be applied to the present problem.

At first, a spherical particle, radius a, of barium oxide is taken, which may contain the peroxide to some extent, and with this sphere the mode of reaction is considered.

The differential equation of heat conduction may be expressed in the form:

$$\frac{\partial v}{\partial t} = \varkappa \nabla^2 v,$$

where v: temperature (or dissociation pressure),
t: time,
$\varkappa$: thermometric conductivity (or its corresponding quantity);

which becomes, on transformation into polar co-ordinates,

$$\frac{\partial v}{\partial t} = \frac{\varkappa}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial v}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial v}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 v}{\partial \phi^2}\right].$$

Initial condition: At the beginning of the reaction, the pressure of active oxygen in the gaseous phase, v_0, has the same value all over the surface of the particle and remains constant throughout the reaction. The sample is at first a uniform solid solution of barium oxide and peroxide, that is, the dissociation pressure is the same at every point of the sample. Let this initial dissociation pressure be denoted by v_s.

Boundary condition: The quantity of oxygen which flows across a unit area of the surface of the sphere during a time interval dt is given by

$$-K\left(\frac{\partial v}{\partial r}\right)_{r=a} dt.$$

On the other hand, the quantity of oxygen which is absorbed from outside through a unit area of the surfaee during the time interval dt is given by

$$H\ (v_0 - v)\ dt,$$

where H is a constant whose value is dependent upon the nature of the surface, v_0 is the pressure of active oxygen in the gaseous phase and v is the decomposition pressure at the surface. In the theory of heat conduction the same expression is also employed which is a fundamental law. But in the present case, the expression may be deduced in the following way.

Consider a very thin film of oxide solid solution around the sphere, where the formation and decomposition of the peroxide are supposed to proceed according to the law of mass action, which may perhaps be justifiable. Since the concentration of the peroxide is proportional to the decomposition pressure, the molar fraction of the peroxide and of the oxide in the thin film may be represented by cv and $1-cv$ respectively, where c is a proportionality constant. Let α or β be the velocity constant of the formation or the decomposition of the peroxide. Then we have, as the rate of absorption of oxygen

$$\alpha(1-cv)-\beta cv.$$

When the sphere attains its equilibrium state, v becomes v_0 and oxygen is absorbed no more.

Hence,

$$\alpha(1-cv_0)-\beta cv_0=0,$$

or

$$\beta=\frac{\alpha(1-cv_0)}{cv_0}.$$

Substituting this value of β in the former expression, we obtain the expression:

$$\alpha(1-cv)-\frac{\alpha(1-cv_0)cv}{cv_0},$$

or

$$\frac{\alpha}{v_0}(v_0-v),$$

or

$$H'(v_0-v),$$

which is a quantity proportional to the rate of absorption of oxygen above considered.

Now the following equation must hold:

$$K\frac{\partial v}{\partial r}=H(v_0-v) \qquad \text{at } r=a,$$

or

$$\frac{\partial v}{\partial r}+h(v-v_0)=0 \qquad \text{at } r=a,$$

where

$$h=\frac{H}{K}.$$

The résumé of what has been mentioned is as follows:

The pressure of active oxygen in the gaseous phase is constant everywhere and remains so during the whole reaction.

As the initial condition we have

$$v=v_s \qquad \text{at } t=0.$$

As the boundary condition we have

$$\frac{\partial v}{\partial r}+h(v-v_0)=0 \qquad \text{at } r=a.$$

As the fundamental differential equation, we have a simpler form

$$\frac{\partial v}{\partial t}=\varkappa\left(\frac{\partial^2 v}{\partial r^2}+\frac{2}{r}\frac{\partial v}{\partial r}\right) \qquad 0<r<a,$$

for v is independent of ϕ and θ.

Putting

$$(v-v_0)r=u,$$

we get

$$\frac{\partial u}{dt} = \varkappa \frac{\partial^2 u}{\partial r^2} \qquad 0 < r < a; \tag{1}$$

$$u = 0 \qquad \text{at } r = 0; \tag{2}$$

$$\frac{\partial u}{\partial r} + \left(h - \frac{1}{a}\right) u = 0 \qquad \text{at } r = a; \tag{3}$$

$$u = r(v_s - v_0) \qquad \text{at } t = 0. \tag{4}$$

Now the expression

$$e^{-\varkappa \alpha^2 t} \sin \alpha r$$

satisfies the first and the second relations but in order to satisfy the third relation, the equation

$$a\alpha \cos a\alpha + (ah - 1) \sin a\alpha = 0 \tag{5}$$

must hold. The values of $a\alpha$ which satisfy the above equation are infinite in number and may be obtained as the common points of the two curves

$$\eta = \tan a\alpha,$$

and

$$\eta = -pa\alpha,$$

where

$$p = \frac{1}{ah - 1}.$$

Let α_1, α_2, α_3,.....be the positive values thus obtained, arranged in the ascending order of their magnitude.

Then the infinite series

$$\sum_{n=1}^{\infty} A_n e^{-\varkappa \alpha_n^2 t} \sin \alpha_n r$$

satisfies the third relation; and the fourth relation may also be satisfied if

$$r(v_s - v_0) = \sum_{n=1}^{\infty} A_n \sin \alpha_n r,$$

where A's are the constants to be determined so that this relation may be satisfied.

For this purpose the following two relations are used:

$$\int_0^a \sin \alpha_m r \sin \alpha_n r \, dr = 0 \qquad m \neq n,$$

and

$$\int_0^a \sin^2 \alpha_n r \, dr = \frac{a}{2} \cdot \frac{a^2\alpha_n^2 + ah(ah-1)}{a^2\alpha_n^2 + (ah-1)^2}.$$

which may easily be proved by taking into account the equation (5).

Suppose $r(v_s - v_o)$ be expanded in a series

$$r(v_s - v_o) = A_1 \sin \alpha_1 r + A_2 \sin \alpha_2 r + \ldots\ldots$$

Multiplying both sides by $\sin \alpha_n r$ and integrating from zero to a with respect to r, we obtain

$$A_n = \frac{2}{a} \cdot \frac{a^2\alpha_n^2 + (ah-1)^2}{a^2\alpha_n^2 + ah(ah-1)} \int_0^a r(v_s - v_o) \sin \alpha_n r \, dr$$

$$= \frac{2ah(v_s - v_o)\sqrt{a^2\alpha_n^2 + (ah-1)^2}}{\alpha_n\{a^2\alpha_n^2 + ah(ah-1)\}}.$$

Hence as the expression which satisfies the relations (1) to (4), we have

$$u = \sum_{n=1}^{\infty} \frac{2ah(v_s - v_o)\sqrt{a^2\alpha_n^2 + (ah-1)^2}}{\alpha_n\{a^2\alpha_n^2 + ah(ah-1)\}} e^{-\kappa\alpha_n^2 t} \sin \alpha_n r,$$

which gives, on transformation of u into v by the relation

$$u = r(v - v_o),$$

$$v = v_o + \sum_{n=1}^{\infty} \frac{2ah(v_s - v_o)\sqrt{a^2\alpha_n^2 + (ah-1)^2}}{r\alpha_n\{a^2\alpha_n^2 + ah(ah-1)\}} e^{-\kappa\alpha_n^2 t} \sin \alpha_n r.$$

Differentiating v with respect to r at $r = a$, we have

$$\left(\frac{\partial v}{\partial r}\right)_{r=a} = \sum_{n=1}^{\infty} \frac{2ah^2(v_o - v_s)}{a^2\alpha_n^2 + ah(ah-1)} e^{-\kappa\alpha_n^2 t},$$

for

$$\frac{\partial}{\partial r}\left(\frac{\sin \alpha_n r}{r}\right)_{r=a} = \frac{-\alpha_n h}{\sqrt{a^2\alpha_n^2 + (ah-1)^2}}.$$

But the expression

$$-K\left(\frac{\partial v}{\partial r}\right)_{r=a}$$

represents the quantity of oxygen which flows in the positive direction of r across a unit area of the surface of the sphere in a unit of time.

$+K\left(\frac{\partial v}{\partial r}\right)_{r=a}.4\pi a^2$ is, therefore, the rate of absorption of oxygen by the sphere through its whole surface, that is to say, the rate of increase of weight of the sphere which we denote by $\frac{dm}{dt}$.

Hence the relation:

$$\frac{dm}{dt}=K\sum_{n=1}^{\infty}\frac{2ah^2(v_o-v_s)}{a^2\alpha_n^{\,2}+ah(ah-1)}e^{-\chi\alpha_n^{\,2}t}.4\pi a^2.$$

Integrating this expression with respect to t from o to ∞, we obtain the final weight increase of the sphere, denoted by m_o,

$$\int_{t=o}^{t=\infty}dm=m_o=\sum_{n=1}^{\infty}\frac{8K\pi a^3h^2(v_o-v_s)}{a^2\alpha_n^{\,2}+ah(ah-1)}\int_o^{\infty}e^{-\chi\alpha_n^{\,2}t}dt$$

$$=\sum_{n=1}^{\infty}\frac{8K\pi a^3h^2(v_o-v_s)}{a^2\alpha_n^{\,2}+ah(ah-1)}\cdot\frac{1}{\chi\alpha_n^{\,2}},$$

or putting

$$m_n\equiv\frac{8K\pi a^3h^2(v_o-v_s)}{a^2\alpha_n^{\,2}+ah(ah-1)}\cdot\frac{1}{\chi\alpha_n^{\,2}},$$

we get

$$m_o=\sum_{n=1}^{\infty}m_n.$$

Finally we obtain as the expression of m in terms of t

$$m=m_o-\sum_{n=1}^{\infty}m_ne^{-\chi\alpha_n^{\,2}t},$$

which gives on differentiation

$$\frac{dm}{dt}=\sum_{n=1}^{\infty} m_n \varkappa a_n^2 \; e^{-\varkappa a_n^2 t}.$$

Here we may regard dm/dt as a function of m, for both dm/dt and m are the functions of a parameter t.

Now it is necessary to investigate the shape of the curve

$$\frac{dm}{dt}=f(m).$$

We have obtained

$$\frac{dm}{dt}=m_1 \varkappa a_1^2 e^{-\varkappa a_1^2 t}+m_2 \varkappa a_2^2 e^{-\varkappa a_2^2 t}+m_3 \varkappa a_3^2 e^{-\varkappa a_3^2 t}+\ldots\ldots,$$

from which we deduce

$$\frac{dm}{dt}=\varkappa a_1^2\left\{m_1 e^{-\varkappa a_1^2 t}+\frac{a_2^2}{a_1^2} m_2 e^{-\varkappa a_2^2 t}+\frac{a_3^2}{a_1^2} m_3 e^{-\varkappa a_3^2 t}+\ldots\ldots\right\},$$

$$=\varkappa a_1^2\left\{m_1 e^{-\varkappa a_1^2 t}+m_2 e^{-\varkappa a_2^2 t}+m_3 e^{-\varkappa a_3^2 t}+\ldots\ldots\right.$$

$$\left.+\frac{a_2^2-a_1^2}{a_1^2} m_2 e^{-\varkappa a_2^2 t}+\frac{a_3^2-a_1^2}{a_1^2} m_3 e^{-\varkappa a_3^2 t}+\ldots\ldots\right\},$$

$$=\varkappa a_1^2 \sum_{n=1}^{\infty} m_n e^{-\varkappa a_n^2 t}+\sum_{n=1}^{\infty} \varkappa (a_n^2-a_1^2) m_n e^{-\varkappa a_n^2 t}.$$

Finally substituting the relation

$$\sum_{n=1}^{\infty} m_n e^{-\varkappa a_n^2 t}=m_0-m$$

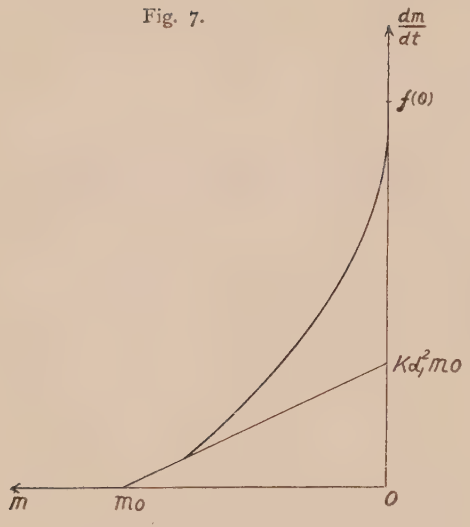
in the above equation, we get

$$\frac{dm}{dt}=\varkappa a_1^2 (m_0-m)+\sum_{n=1}^{\infty} \varkappa (a_n^2-a_1^2) m_n e^{-\varkappa a_n^2 t}.$$

Taking the first term of the right hand side of the equation, we get an equation linear with respect to dm/dt and m:

$$\frac{dm}{dt}=\varkappa a_1^2 (m_0-m),$$

Fig. 7.



which represents a straight line of inclination $-\varkappa a_1^2$; (cf. the accompanying figure, Fig. 7).

Next, the second term is always a positive quantity, for a_n^2 is always greater than a_1^2, and moreover, it converges rapidly to zero as t increases. But since t and m increase side by side, the second term becomes smaller and smaller as m increases. Geometrically this means that the curve

$$\frac{dm}{dt}=f(m)$$

approaches the straight line

$$\frac{dm}{dt}=\varkappa a_1^2(m_0-m)$$

as m increases. Moreover, that the curve touches the straight line at $m=m_0$ or at $t=\infty$ may be proved as follows:

The inclination of a tangent to the curve is given by the expression

$$\frac{d(dm/dt)}{dm}=\frac{d^2m}{dt^2}\Big/\frac{dm}{dt}$$

$$=\frac{-m_1\varkappa^2a_1^4e^{-\varkappa a_1^2t}-m_2\varkappa^2a_2^4e^{-\varkappa a_2^2t}-m_3\varkappa^2a_3^4e^{-\varkappa a_3^2t}-\cdots\cdots}{m_1\varkappa a_1^2e^{-\varkappa a_1^2t}+m_2\varkappa a_2^2e^{-\varkappa a_2^2t}+m_3\varkappa a_3^2e^{-\varkappa a_3^2t}+\cdots\cdots};$$

dividing both the denominator and the numerator by

$$m_1\varkappa a_1^2e^{-\varkappa a_1^2t},$$

we get

$$\frac{d(dm/dt)}{dm}=\frac{-\varkappa a_1^2-\varkappa\dfrac{m_2a_2^4}{m_1a_1^2}e^{-\varkappa(a_2^2-a_1^2)t}-\varkappa\dfrac{m_3a_3^4}{m_1a_1^2}e^{-\varkappa(a_3^2-a_1^2)t}-\cdots\cdots}{1+\dfrac{m_2a_2^2}{m_1a_1^2}e^{-\varkappa(a_2^2-a_1^2)t}+\dfrac{m_3a_3^2}{m_1a_1^2}e^{-\varkappa(a_3^2-a_1^2)t}+\cdots\cdots}.$$

Now putting $t=\infty$ in this expression, we obtain the inclination of the tangent to the curve at $m=m_0$:

$$\left[\frac{d(dm/dt)}{dm}\right]_{m=m_o} = -\varkappa a_1^2,$$

which is equal to the inclination of the straight line

$$\frac{dm}{dt} = \varkappa a_1^2 (m_o - m). \qquad q.\,e.\,d.$$

The tangent to the curve at $m=0$ or at $t=0$ must, in the next, be considered.

The inclination of this tangent may be given by

$$\left[\frac{d(dm/dt)}{dm}\right]_{m=0} = \left[\frac{d^2m}{dt^2} \Big/ \frac{dm}{dt}\right]_{t=0}$$

$$= \frac{-m_1\varkappa^2 a_1^4 - m_2\varkappa^2 a_2^4 - m_3\varkappa^2 a_3^4 - \ldots\ldots}{m_1\varkappa a_1^2 + m_2\varkappa a_2^2 + m_3\varkappa a_3^2 + \ldots\ldots},$$

or substituting the values of m's,

$$= \frac{\sum_{n=1}^{\infty} \frac{-\varkappa a_n^2}{a^2 a_n^2 + ah(ah-1)}}{\sum_{n=1}^{\infty} \frac{1}{a^2 a_n^2 + ah(ah-1)}}.$$

But the numerator is a divergent series while the denominator converges to a finite number.

Hence the conclusion that the tangent to the curve at $m=0$ is the dm/dt—axis itself.

From these properties above mentioned, it is now possible to form an idea about the shape of the curve: the curve touches the dm/dt-axis at $m=0$ and always lies above the straight line

$$\frac{dm}{dt} = \varkappa a_1^2 (m_o - m)$$

which it touches at $m=m_o$, (cf. Fig. 7).

It is now necessary to investigate how the shape of the curve will change when a is made very small. In this case the value of m_o decreases much more rapidly than the value of $(dm/dt)_{m=0}$ does and the inclination of the tangent to the curve at $m=m_o$ becomes greater.

It may, therefore, be concluded that the curve diminishes its curvature and tends to a straight line, as the radius of the sphere becomes smaller.

If it now be assumed with approximation that the curve becomes a straight line for a very small but finite value of the radius, we obtain a much simplified equation for the curve:

$$\frac{dm}{dt}=k(m_o-m),$$

which indicates that the reaction between a small solid sphere and a gas may be regarded approximately as a homogeneous monomolecular reaction, the pressure of the gas being constant.

Now turning away from the mathematical treatment, we will now consider the physical side of this problem.

The area of the surface of a sphere is proportional to the square of its radius while the volume is to the cube.

When the radius becomes sufficiently small, the volume may be neglected against the surface area. With our sphere of barium oxide, this means that almost all the oxide molecules reside on the surface layer where, as has already been assumed, the absorption of oxygen goes on according to the law of mass action. Hence the reaction occurring between a small sphere and a gaseous substance may be regarded as a homogeneous one.

This conclusion is, as may be expected, the same as that obtained by the mathematical reasoning.

In the following, it is intended to investigate the total aspect of the reaction, when these small oxide particles begin to react one after the other, applying, thereby, the simplified formula to the reaction of each particle.

Now let a number of the oxide spheres, n_o, begin to react all at once.

The equation of the reaction is given by

$$\frac{dm}{dt}=k(n_om_o-m),$$

which represents a straight line with an inclination $-k$ and with intercepts n_om_o and kn_om_o on the co-ordinate axes, (cf. Fig. 8).

At a time $t=t_o$ let n more of fresh spheres begin to react, the equation of which reaction is given by

$$\frac{dm'}{dt'}=k(nm_o-m'),$$

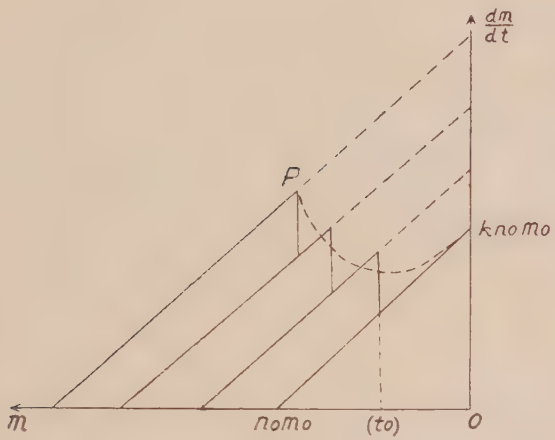


Fig. 8.

where m' denotes the weight increase of the n spheres at a time t' which is connected with t by the relation

$$t = t' + t_o ;$$

hence $dt = dt'$.

The total rate of weight increase of the $n+n_o$ spheres at a time t when the total weight increase is $m+m'$, is given by

$$\frac{dm}{dt} + \frac{dm'}{dt'} = \frac{d(m+m')}{dt} = k\Big[(n+n_o)m_o - (m+m')\Big].$$

Let $m+m'$ be simply denoted by m which is the total weight increase of all the spheres; then we have

$$\frac{dm}{dt} = k\Big[(n+n_o)m_o - m\Big].$$

From this equation it is clear that, at the time when the n fresh spheres begin to react, the value of dm/dt increases suddenly from $k(n_o m_o - m)$ to $k[(n+n_o)m_o - m]$, that is, by the amount knm_o, and after this time the point $(dm/dt, m)$ describes a straight line with an inclination $-k$, as if $n+n_o$ spheres had begun to react all at once at $t=0$, (cf. Fig. 8).

Now suppose again that n' more of fresh spheres begin to react at a time $t=t_o'$, and so on. The value of dm/dt will accordingly increase by the amount $kn'm_o$, etc. at each time and from that time on dm/dt changes with m, as if the reacting spheres had existed from the very beginning of the reaction, *i.e.* at $t=0$ or at $m=0$, wholly independent of how and when the number of reacting spheres had increased.

Hence we have a general equation:

$$\frac{dm}{dt} = k\Big[(n+n_o)m_o - m\Big],$$

where $n+n_o$ is the number of the reacting spheres which exist when

the total weight increase is m, and n may increase according to any law.

In the above equation, both n and n_o are integers, but if n_o is sufficiently large and the change of n is always very small when compared with n_o, $n+n_o$ may be regarded as a continuous variable. The equation will, therefore, represent a smooth continuous curve, which is illustrated in the preceding figure, (Fig. 8).

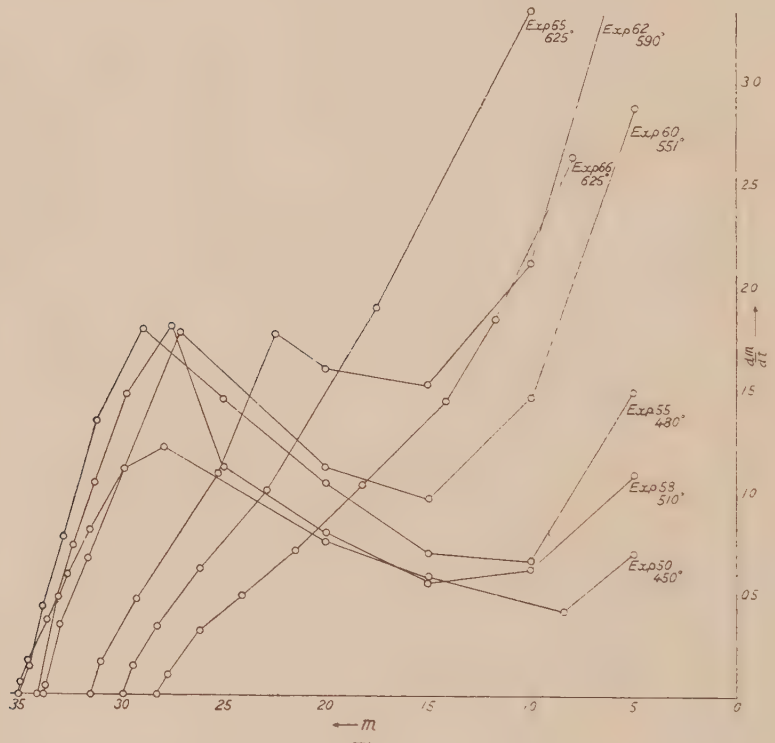


Fig. 9.

Now are required the $dm/dt-m$ curves as derived from the experimental data. They are shown in the accompanying figure, Fig. 9. The values of dm/dt were determined geometrically from the graph of $m-t$ curves. In the earlier portion of the curves, exact values of dm/dt are not to be determined, which are all rejected.

By precisely examining these experimental curves and the properties of the theoretical curve side by side, the following assumptions were found to be necessary in order to explain the experimental results quantitatively :—

The sample of barium oxide consists of a very large but finite number of small spheres of equal size.

At the beginning of the reaction, some of these spheres are in a state ready to react with oxygen.

When the reaction once commences, the remaining spheres will enter into reaction one after the other.

The number of the spheres thus become active in a unit of time is proportional to the quantity of the peroxide then already formed.

Some explanatory remarks on these assumptions will be given below.

The sample of barium oxide is a very brittle one and may be crushed into a uniform powder; it may, therefore, be justifiable to assume that the sample consists of this uniform powder, each particle of which is regarded as a small sphere of size equal to each of the remainder.

The surface of the sample is very coarse being covered with small oxide particles. These particles may, therefore, readily react with oxygen when they come into contact with it at a suitable high temperature.

Probably the formation of the peroxide may not be confined on the surface of the active spheres only, but oxygen may, though very small in quantity, creep deeper into the interior to form a peroxide film on some spheres not yet active. As soon as such a film is formed on the spheres, the adhering power between them will be greatly diminished, for oxygen gas is constantly entering and leaving their surfaces. Consequently there occurs a loosening of particles, cracks being formed between them. Through these cracks, however, oxygen can now flow in quite freely and some fresh particles thus begin to react with oxygen of pressure v_0, that is, they become active. The time rate of such an activation of particles may be assumed to be proportional to the quantity of the peroxide which is, as above mentioned, formed on the spheres not yet normally active. This quantity of the peroxide may, in turn, be assumed to be a certain fraction, though very small, of the quantity of oxygen m then already absorbed by the active spheres.

Hence the time rate of increase of n is proportional to m, that is, when mathematically expressed,

$$\frac{dn}{dt} = Am, \quad \text{where } A \text{ is a proportionality constant.}$$

As soon as all the spheres become active in this manner, the activation stops at once, that is, dn/dt becomes zero suddenly.

From this moment forward, the absorption of oxygen becomes less and less energetic till at last the reaction arrives at equilibrium.

As stated in Gmelin-Kraut's Handbuch der anorganischen Chemie[1], barium peroxide diminishes its volume considerably when heated. This fact may be accounted for by the following assumption: the particles of the solid mass loosened by cracking in the course of formation of barium peroxide from oxide begin to unite into a more compact mass as the peroxide is decomposed by heating and the liberated oxygen escapes from it. Thus when the oxygen content of the mass has diminished to the initial value, the sample has now returned to its original state more or less completely. For this reason the experimental curves belonging to the same temperature show an almost identical form.

It is now attempted to explain qualitatively the form of the curves experimentally obtained.

The slope of the $m-t$ curves for small values of t is very steep, or when m is small the value of dm/dt is very great. This may be explained by the assumption that there exists a large number of the spheres ready to react at the beginning of the reaction.

But since the activation is not so predominant in the earlier period of the reaction, this portion of the $m-t$ curves is convex upward and the $dm/dt-m$ curves are here decreasing. By and by, however, the activation becomes more and more energetic as m increases, in consequence of which the $m-t$ curves turn into concave upward and the $dm/dt-m$ curves begin to rise. But the number of the spheres being finite, the activation will suddenly stop as soon as all the spheres are activated. The maximum point of the $dm/dt-m$ curve corresponds to this point where the curve changes its direction suddenly and falls down in a direct line to cut the m-axis at the point $m=M$, the final weight increase of the sample. Accordingly the $m-t$ curve becomes again convex upward and remaining so, approaches a horizontal line.

The curves obtained at lower temperatures are the examples of such a type of reaction.

The curves obtained at 625° have, however, no maximum point nor the second inflexional point. This may be explained as follows:—

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[1] 7th Ed., II, II, p. 21.

In these cases, the number of the spheres initially active being very large, the remainder, a comparatively small part of the spheres, becomes all active before the activation attains its full manifestation.

Hereafter the quantitative side of the problem will be considered.

According to the assumptions previously mentioned, the reaction must proceed satisfying the following two equations:

$$\frac{dm}{dt}=k\Big[(n+n_0)m_0-m\Big]$$

and

$$\frac{dn}{dt}=Am.$$

Let the final weight increase of a particle be m_0 and that of the sample be M. Then the total number of the spheres contained in the sample is

$$N=\frac{M}{m_0}.$$

In the above equations, since N is a finite number, n can not increase without limit but becomes a constant when n reaches the value $N-n_0$, that is to say, the number of the active spheres increases no more as soon as the whole spheres contained in the sample begin to react. From this moment forward, therefore, the simultaneous equations may be replaced by a single equation

$$\frac{dm}{dt}=k(M-m),$$

which is obtained by substituting the relations

$$\frac{dn}{dt}=0,$$

and

$$n=N-n_0 \text{ or } (n+n_0)m_0=M,$$

in the preceding equations.

Now it is required to solve the simultaneous equations:

(1)
$$\frac{dm}{dt}=k\Big[(n+n_0)m_0-m\Big],$$

(2)
$$\frac{dn}{dt}=Am.$$

Differentiating (1) with respect to t, we have

$$\frac{d^2m}{dt^2}=k\left[m_0\frac{dn}{dt}-\frac{dm}{dt}\right],$$

Substituting (2) in this equation, we have

$$\frac{d^2m}{dt^2}+k\frac{dm}{dt}-m_0Akm=0, \tag{3}$$

the auxiliary equation of which is

$$\xi^2+k\xi-m_0Ak=0.$$

Solving with respect to ξ, we get

$$\xi=\frac{-k\pm\sqrt{k^2+4m_0Ak}}{2}.$$

But since $m_0>0$, $A>0$ and $k>0$,

the values of ξ are real and distinct.

The general solution is, therefore,

$$m=c_1e^{\frac{-k+\sqrt{k^2+4m_0Ak}}{2}t}+c_2e^{\frac{-k-\sqrt{k^2+4m_0Ak}}{2}t}. \tag{4}$$

The integration constants c_1 and c_2 are to be determined by the initial conditions

$$n=0 \text{ and } m=0, \text{ at } t=0.$$

Hence we get from (4)

$$c_1+c_2=0. \tag{5}$$

Differentiating (4) with respect to t, we have

$$\frac{dm}{dt}=c_1\frac{-k+\sqrt{k^2+4m_0Ak}}{2}e^{\frac{-k+\sqrt{k^2+4m_0Ak}}{2}t}+c_2\frac{-k-\sqrt{k^2+4m_0Ak}}{2}e^{\frac{-k-\sqrt{k^2+4m_0Ak}}{2}t}.$$

Putting $t=0$ in this equation, we have the value of $\left(\frac{dm}{dt}\right)_{t=0}$.

But from (1) we get the value of $\left(\frac{dm}{dt}\right)_{m=0}$ by putting $m=0$ and $n=0$.

But since

$$\left(\frac{dm}{dt}\right)_{m=0} = \left(\frac{dm}{dt}\right)_{t=0},$$

we have

$$m_0 n_0 k = c_1 \frac{-k+\sqrt{k^2+4m_0Ak}}{2} + c_2 \frac{-k-\sqrt{k^2+4m_0Ak}}{2},$$

which gives, when simplified by the relation (5),

$$m_0 n_0 k = c_1 \sqrt{k_2+4m_0Ak}.$$

$$\therefore \quad c_1 = -c_2 = \frac{m_0 n_0 k}{\sqrt{k^2+4m_0Ak}}.$$

Substituting these values of the integration constants in (4), we have finally the solution:

$$\text{(A)} \qquad m = A_0 \frac{1}{2}\left[e^{(-\frac{k}{2}+B_0)t} - e^{(-\frac{k}{2}-B_0)t}\right],$$

or

$$\text{(A')} \qquad m = A_0 e^{-\frac{k}{2}t} \sinh B_0 t,$$

where

$$A_0 = \frac{2m_0 n_0 k}{\sqrt{k^2+4m_0Ak}},$$

$$B_0 = \frac{\sqrt{k^2+4m_0Ak}}{2}.$$

From the differential equation

$$\frac{dm}{dt} = k(M-m)$$

we have at once

$$\text{(B)} \qquad m = M(1-e^{-kt}).$$

The increase of weight of the sample at a time t is given by equation (A), but after all the spheres have begun to react, the weight increase is given by equation (B).

It must be noticed here that t in (A) and t in (B) are not the same variable but they are connected by a relation soon afterward to be obtained.

It is now necessary to determine the point of transition from (A) to (B) which corresponds to the point P in the figure on page 37. At this point we have the condition that the value of dm/dt or m of each equation is equal to one another. These values, however, are not to be determined by mere transformations of the equations. A graphical method will serve here.

On differentiation of equation (A), we get

$$\text{(C)}\quad \frac{dm}{dt}=\frac{A_0}{2}\left[\left(-\frac{k}{2}+B_0\right)e^{\left(-\frac{k}{2}+B_0\right)t}+\left(\frac{k}{2}+B_0\right)e^{\left(-\frac{k}{2}-B_0\right)t}\right].$$

By substituting suitable numerical values of t in (A) and (C), we obtain some pairs of values m and dm/dt. These pairs are then plotted on a co-ordinate plane $(m, dm/dt)$. The points thus obtained are connected by a smooth curve. On the other hand a straight line which corresponds to equation (B), in the differentiated form, is drawn on the same plane. Then the co-ordinates of the point of intersection of these two curves are what we required. Let this value of m be denoted by μ and the corresponding value of t in (A) or (B) be denoted by τ or τ_0 respectively.

This graphical method may, however, be replaced by a simpler method provided that the following approximation is allowed.

If the value of τ is sufficiently large, the second term of the right hand side of equation (A) or (C) may be neglected against the first.

In such a case we have the following simple equations for m and dm/dt:

$$m=\frac{A_0}{2}e^{\left(-\frac{k}{2}+B_0\right)t}$$

and

$$\frac{dm}{dt}=\frac{A_0}{2}\left(-\frac{k}{2}+B_0\right)e^{\left(-\frac{k}{2}+B_0\right)t}$$

Substituting the former in the latter, we have

$$\text{(D)}\qquad \frac{dm}{dt}=\left(-\frac{k}{2}+B_0\right)m.$$

Now for the point of transition, the values of dm/dt of (A) or (D) and of (B) must be the same. Hence

$$k(M-\mu)=\left(-\frac{k}{2}+B_0\right)\mu,$$

or $$\mu = \frac{kM}{\frac{k}{2} + B_0}.$$

Now τ may be calculated by substituting this value of μ in the approximated equation of m or more easily be obtained by using the graph of (A), and τ_0 may be calculated from (B):

$$\mu = M\left(1 - e^{-k\tau_0}\right)$$

or $$\tau_0 = \frac{\log \frac{M-\mu}{M}}{-k}.$$

Now it is clear that t in (A), t_A, and t in (B), t_B, may be connected by the relation

$$t_B = t_A - (\tau - \tau_0).$$

Hence equation (B) is transformed into

$$m = M\left(1 - e^{-k[t-(\tau-\tau_0)]}\right).$$

As the result of all what has hitherto been discussed, the course of the reaction may be represented by the following two equations, the interval of the variable t being taken as indicated therewith:

(I) $$m = \frac{A_0}{2}\left[e^{(-\frac{k}{2}+B_0)t} - e^{(-\frac{k}{2}-B_0)t}\right],$$

or

(I′) $$m = A_0 e^{-\frac{k}{2}t} \sinh B_0 t; \qquad t: 0 \longrightarrow \tau.$$

(II) $$m = M(1 - e^{-k[t-(\tau-\tau_0)]}); \qquad t: \tau \longrightarrow \infty.$$

A word about the physical meaning of the equations.

In the early period of the reaction, the weight increase of the sample (a) is represented by (I). At the time $t = \tau - \tau_0$, a hypothetical sample (b), whose particles are all active from the beginning of the reaction, commences its reaction. The weight increase of this sample is represented by (II), the interval of t being extended from $\tau \longrightarrow \infty$ to $\tau - \tau_0 \longrightarrow \infty$.

By the time $t = \tau$ the two samples have absorbed the same amount of oxygen, μ, and at this very moment the activation of the spheres

of the sample (a) just ends. From this time on, the rate of absorption of oxygen being the same for both samples, their reactions, taken as a whole, proceed perfectly in the same manner, and may be represented by the single equation (II).

Equation (I) with the variable $t>\tau$ may have a physical meaning provided that the sample (a) contains an infinite number of spheres to be activated. In reality this not being the case, (I) loses its meaning from the time $t=\tau$ forward. Though, taken as a whole, the course of increase of weight is the same for both samples from the time τ on, a great difference will be found when the state of every particle of each sample is compared with each other. Indeed, all particles of the sample (b) are always exactly in the same state, while, with the sample (a), the state of reaction is different in each individual particle, some being vigorously reacting, some being about to die away.

In the next, the shape of the curves must be examined.

From equation (I), we obtain, on differentiation,

$$\frac{dm}{dt}=\frac{A_0}{2}\left[\left(-\frac{k}{2}+B_0\right)e^{\left(-\frac{k}{2}+B_0\right)t}+\left(\frac{k}{2}+B_0\right)e^{\left(-\frac{k}{2}-B_0\right)t}\right]$$

in which every term of the right hand side being greater than zero, dm/dt is always positive. That is to say, the curve is always rising.

Differentiating again, we get

$$\frac{d^2m}{dt^2}=\frac{A_0}{2}\left(-\frac{k}{2}+B_0\right)^2e^{\left(-\frac{k}{2}+B_0\right)t}-\left(\frac{k}{2}+B_0\right)^2e^{\left(-\frac{k}{2}-B_0\right)t}.$$

Then

$$\frac{d^2m}{dt^2}=0 \quad \text{if} \quad \frac{(k+2B_0)^2}{(-k+2B_0)^2}e^{-2B_0t}=1.$$

The value of t, denoted by t_0, which satisfies the relation, may always be found and it is a positive quantity, for

$$\frac{(k+2B_0)^2}{(-k+2B_0)^2}>1 \quad \text{and} \quad B_0>0.$$

Moreover,

$$\frac{d^2m}{dt^2}\gtrless 0 \text{ according as } t\lessgtr t_0.$$

Hence the curve is convex upward for $t<t_0$ and concave upward for $t>t_0$, and consequently it has a point of inflexion at $t=t_0$.

That this inflectional point corresponds to the minimum point of the $dm/dt - m$ curve may be proved as follows:

The inclination of a tangent to the $dm/dt - m$ curve is given by

$$\frac{d(dm/dt)}{dm} \quad \text{or} \quad \frac{d^2m}{dt^2} \Big/ \frac{dm}{dt}.$$

At the point of inflection, dm/dt has a certain positive value. Let the value of m corresponding to t_o be μ_o, then

$$\frac{d^2m}{dt^2} \Big/ \frac{dm}{dt} \gtrless 0 \quad \text{according as } t \gtrless t_o,$$

or

$$\text{according as } m \gtrless \mu_o.$$

Hence the proposition.

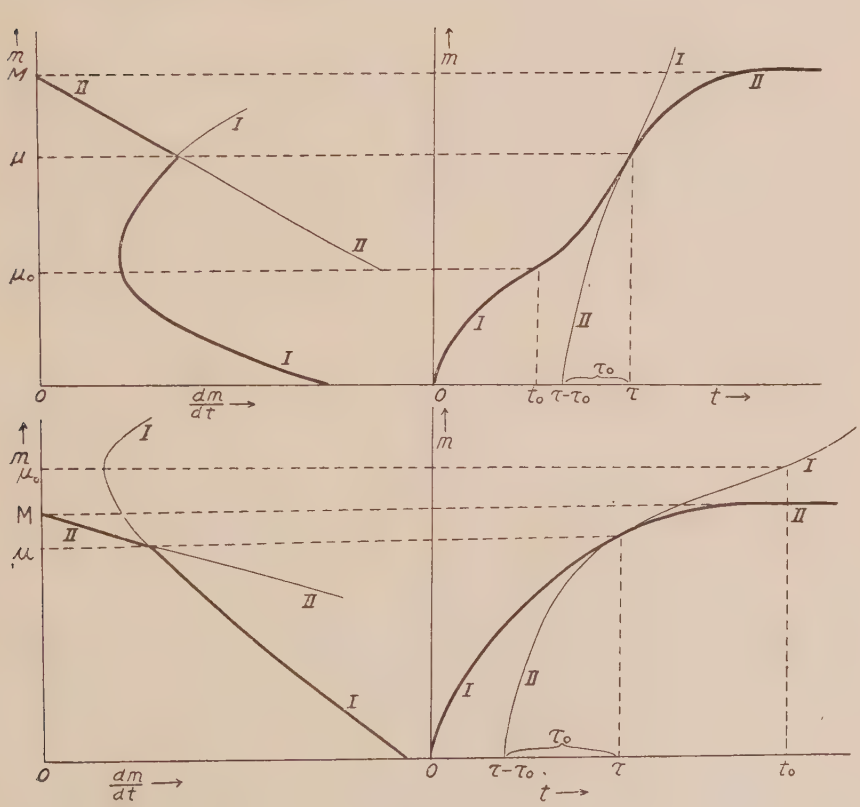


Fig. 10.

It was previously mentioned that the curve (I) loses its physical meaning at $t=\tau$ to be followed by the curve (II).

According to the magnitude of τ and t_o, the resulting curve will assume a very different shape.

When $\tau > t_o$, *i. e.* when the point of connection of the curves (I) and (II) is preceded by the point of inflection of (I). In this case, the curve (I) is concave upward at $t=\tau$ and the curve (II) is always convex upward, hence the point of connection is an inflectional point. As was previously mentioned, at the point of connection, dm/dt has the same value for both curves (I) and (II). It is, therefore, obvious that these curves touch each other at this point. Thus the resulting curve has two points of inflection in all.

When $\tau < t_o$, *i.e.* when the point of connection is followed by the point of inflection of (I). In this case the curves being both convex upward at $t=\tau$, no inflectional point results from the connection. The resulting curve, therefore, has no such point at all. See the two accompanying figures, (Fig. 10).

Now it remains only to determine the constants in the equations (I) and (II) from the experimental data. The examples of these determinations are collected in the next chapter.

For the sake of convenience, the equations are here rewritten:

$$\text{(I)} \qquad m=\frac{A_o}{2}\left[e^{(-\frac{k}{2}+B_o)t}-e^{(-\frac{k}{2}-B_o)t}\right]$$

or

$$\text{(I')} \qquad m=A_o e^{-\frac{k}{2}t}\sinh B_o t\,; \qquad t:0\longrightarrow\tau,$$

and

$$\text{(II)} \qquad m=M\left(1-e^{-k[t-(\tau-\tau_o)]}\right); \qquad t:\tau\longrightarrow\infty,$$

where $A_o=\dfrac{2m_o n_o k}{\sqrt{k^2+4m_o Ak}}$; and $B_o=\dfrac{\sqrt{k^2+4m_o Ak}}{2}$.

Determination of k.—From equation (II), we get

$$\frac{dm}{dt}=k(M-m),$$

which represents a straight line with an inclination of $-k$. By a graphical method several sets of values of $(dm/dt,\ m)$ are determined from

the latter part of the experimental $m-t$ curve. These sets are then plotted on a co-ordinate plane $(dm/dt, m)$. If the theory is correct, these points must lie on a single straight line, whose inclination is what is required, *i.e.* $-k$.

Determination of A_0.—For sufficiently large values of t, the second term of equation (I) may be neglected in comparison with the first. So we may obtain, by taking common logarithms of both sides:

$$\log m = \log A_0 + \log \frac{1}{2} - \frac{k}{2} \log e.t + B_0 \log e.t,$$

which is a linear function with respect to $\log m$ and t.

The experimental curve $\log m-t$ curve must, therefore, approach a straight line as t increases.

Putting $t=0$ in the above equation, we get

$$[\log m]_{t=0} = \log A_0 + \log \frac{1}{2}$$

or

$$\log A_0 = [\log m]_{t=0} - \log \frac{1}{2}.$$

By this relation, the value of A_0 may be calculated, for the value of $[\log m]_{t=0}$ is determined as a point of intersection of the $\log m$-axis with the straight line produced from the rectilinear portion of the experimental $\log m-t$ curve.

Determination of B_0.—From (I′), we have

$$\log m = \log A_0 - \frac{k}{2} \log e.t + \log \sinh B_0 t,$$

or from the simplified equation,

$$\log m = \log A_0 + \log \frac{1}{2} - \frac{k}{2} \log e.t + B_0 \log e.t.$$

By substituting a numerical value of t and that of $\log m$ corresponding to the t in either of the above equations, B_0 may be calculated at once, for A_0 and k are now both known. In this determination, a larger value of t is preferable in order to make the errors as small as possible.

The above methods of determination of A_0 and B_0 are founded on the simplified form of equation (I). But when the negligence of the

second term is not allowed, these methods must fail altogether. In such cases, either of the following methods must be employed.

The impossibility of neglecting the second term means that the $log\, m - t$ curves have no rectilinear portion at all. Hence the determination of $[log\, m]_{t=0}$ is impossible. But with speculation we may draw a straight line, to which the experimental $log\, m - t$ curve, the portion corresponding to (I), may probably tend. Then, with this line, A_0 and B_0 may be determined as was previously done. Now, by giving a preferably small numerical value to t, the corresponding value of m or $log\, m$ is calculated with equation (I) with the constants thus determined. If the calculated and the experimental value do not agree well, we must repeat this trial once more. At most after three or four trials good values of A_0 and B_0 may be arrived at.

Another graphical but more rigorous method is as follows:

From equation (I'), we have

$$log\, m = log\, A_0 + log\, sinh\, B_0 t - \frac{k}{2} log\, e.t,$$

in which A_0 and B_0 are unknown quantities. By substituting two pairs of experimental values, (m', t') and (m'', t''), in the above equation, we have

$$log\, m' = log\, A_0 + log\, sinh\, B_0 t' - \frac{k}{2} log\, e.t'$$

and

$$log\, m'' = log\, A_0 + log\, sinh\, B_0 t'' - \frac{k}{2} log\, e.t'' \qquad (t' > t'').$$

By subtracting the latter from the former, we have

$$log\, m' - log\, m'' = log\, sinh\, B_0 t' - log\, sinh\, B_0 t'' - \frac{k}{2} log\, e.(t' - t'')$$

or

$$log\, sinh\, B_0 t' - log\, sinh\, B_0 t'' = log \frac{m'}{m''} + \frac{k}{2} log\, e.(t' - t'') = K,$$

where K is a constant, the value of which may be calculated from the values m', m', t', t'' and k. It may, perhaps, be impossible to calculate the value of B_0 directly from the last equation. By a graphical method, however, it may easily be obtained.

Consider an expression

$$log\, sinh\, x' - log\, sinh\, x'' = K,$$

where x' and x'' must satisfy the relation

$$\frac{x'}{x''} = \frac{B_0 t'}{B_0 t''} = \frac{t'}{t''}.$$

If we could, by any means, find the values x' and x'' such as satisfy the above two relations, the value of B_0 might be determined by either of the equations:

$$B_0 = x'/t'$$

and

$$B_0 = x''/t''.$$

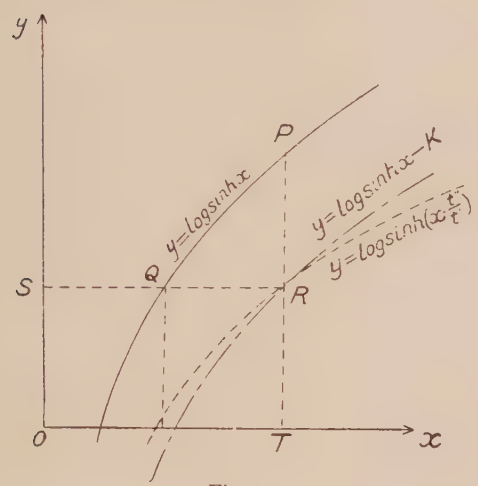


Fig. 11.

Now consider the curve

$$y = \log \sinh x.$$

Let P and Q be the points on this curve which correspond to the two pairs of values:

$$(\log \sinh x', \; x')$$

and

$$(\log \sinh x'', \; x'').$$

Through Q draw a straight line SQR, parallel to the x-axis, meeting the y-axis at S.

Through P draw a straight line PRT, parallel to the y-axis, meeting the x-axis at T. Let R be the point of intersection of these two straight lines.

Then

$$SO = \log \sinh x''$$

and

$$PT = \log \sinh x';$$

$$\therefore PT - SO = PR = \log \sinh x' - \log \sinh x'' = K.$$

Hence, the point R must lie on the curve

$$y = \log \sinh x - K.$$

On the other hand,

$$\frac{SR}{SQ} = \frac{x'}{x''} = \frac{t'}{t''}.$$

Hence, the point R must also lie on the curve

$$y = \log \sinh\left(x\frac{t''}{t'}\right).$$

The point R must, therefore, be a point of intersection of the two curves

$$y = \log \sinh x - K$$

and

$$y = \log \sinh\left(x\frac{t''}{t'}\right).$$

The former curve may be graphically obtained by shifting the curve $y = \log \sinh x$ by a distance K parallel to, and in the negative sense of, the y-axis.

The latter curve may also be graphically obtained by plotting points such as R, so that the relation

$$\frac{SR}{SQ} = \frac{t'}{t''}$$

or

$$\frac{SR - SQ}{SQ} = \frac{QR}{SQ} = \frac{t' - t''}{t''}$$

may be satisfied.

In practice, we take such values of t' and t'' as $t'/t'' = 2$.

In this simple case, since

$$QR = SQ,$$

the point R may easily be plotted by means of a pair of compasses.

It is now necessary to prove that, for given values of t' and t'', a pair of values x' and x'' are to be uniquely determined, that is, that there is one and only one point of intersection of these two curves. If there be any more, indeed, we have no rigorous means of selecting one from among them.

Let $t'/t'' = n$, n being a positive number greater than unity.

In the preceding figure, Fig. 11, $y = \log \sinh x$ is represented by the curve passing through the points P and Q.

SQR is a straight line parallel to the x-axis.

If $SQ = x$ and $SR = nx$, R is a point on the curve

$$y = \log \sinh \frac{x}{n}.$$

We must now investigate the variation of the segment RP with x (RP being parallel to the y-axis).

Consider an expression

$$S \equiv \log \sinh nx - \log \sinh x$$

which corresponds to the segment.

By the definition of the hyperbolic sine, we have

$$\log \sinh nx - \log \sinh x = \log\left(e^{nx} - e^{-nx}\right) - \log\left(e^{x} - e^{-x}\right).$$

Differentiating S with respect to x, we have

$$\frac{dS}{dx} = \frac{ne^{nx} + ne^{-nx}}{e^{nx} - e^{-nx}} - \frac{e^{x} + e^{-x}}{e^{x} - e^{-x}}.$$

Simplifying the expression, we have finally

$$\frac{dS}{dx} = \frac{(n-1)\sinh(n+1)x - (n+1)\sinh(n-1)x}{2 \sinh nx . \sinh x},$$

of which numerator is, when transformed,

$$(n^2-1)\left\{\frac{\sinh(n+1)x}{n+1} - \frac{\sinh(n-1)x}{n-1}\right\}.$$

As the denominator of dS/dx is always positive for $x>0$, it is necessary to know whether the numerator is positive or negative for $x>0$.

Now consider the curve

$$y = \sinh x; \quad \text{for } x>0.$$

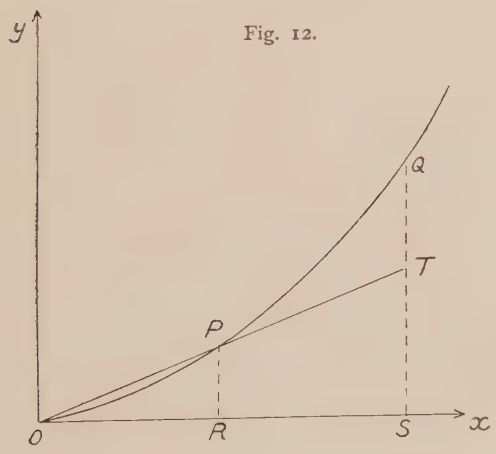


Fig. 12.

In the accompanying figure, Fig. 12, let

$$OR = (n-1)x$$

and $$OS = (n+1)x;$$

and let P and Q be the points on the curve corresponding to R and S respectively.

Then $$PR = \sinh(n-1)x$$

and $$QS = \sinh(n+1)x.$$

Suppose a straight line OPT, passing through the origin of the co-ordinates and the point P on the curve, and cutting the straight line STQ at T.

Now we see that

$$\frac{TS}{PR}=\frac{n+1}{n-1},$$

or

$$\frac{TS}{n+1}=\frac{PR}{n-1}=\frac{sinh(n-1)x}{n-1}.$$

But the curve $y=sinh\,x$ is always concave upward, for

$$\frac{d^2y}{dx^2}=\frac{1}{2}\left(e^x-e^{-x}\right)=sinh\,x$$

is always positive for $x>0$.

Hence, the portion of the straight line, OP, lies above and the portion, PT, lies beneath this curve, there being no other point of intersection except at O and P.

Hence $$QS>TS;$$

but $$QS=sinh(n+1)x;$$

$$\therefore \quad sinh(n+1)x>TS,$$

or $$\frac{sinh(n+1)x}{n+1}>\frac{TS}{n+1},$$

but $$=\frac{sinh(n-1)x}{n-1}$$

$$\therefore \quad \frac{sinh(n+1)x}{n+1}>\frac{sinh(n-1)x}{n-1}.$$

Hence, n^2-1 being always positive for $n>1$, the numerator of dS/dx is always positive for $x>0$, consequently

$$\frac{dS}{dx}>0, \qquad \text{for } x>0 \text{ and } n>1.$$

This means that the segment S is always increasing as x increases in the interval of x: $0\longrightarrow\infty$.

But $$S=log\,sinh\,nx-log\,sinh\,x=log\frac{e^{nx}-e^{-nx}}{e^n-e^{-n}}.$$

Expanding e^{nx} and e^{-nx}, etc. in series, we have

$$e^{nx}=1+\frac{nx}{1}+\frac{(nx)^2}{1.2}+\frac{(nx)^3}{1.2.3}+\ldots\ldots, \qquad \text{for } nx\leq 1.$$

$$e^{-nx}=1-\frac{nx}{1}+\frac{(nx)^2}{1.2}-\frac{(nx)^3}{1.2.3}+\ldots\ldots, \qquad ,,$$

etc.

Hence

$$S=log\frac{\frac{nx}{1}+\frac{(nx)^3}{1.2.3}+\frac{(nx)^5}{1.2.3.4.5}+\ldots\ldots}{\frac{x}{1}+\frac{x^3}{1.2.3}+\frac{x^5}{1.2\,3.4.5}+\ldots\ldots} \qquad \text{for } nx<1.$$

When x tends to zero, the limiting value of S is

$$S=log n.$$

It is obvious that when x tends to infinity, S tends also to infinity.

The segment S, therefore, passes successively once and only once every value ranging from $log\, n$ to infinity, as x changes from zero to infinity.

Hence, if $$K>log\, n,$$

there is one and only one value of S, such as

$$S=log\, sinh\, nx-log\, sinh\, x=K=log\, m'-log\, m''+\frac{k}{2}log\, e.(t'-t''),$$

that is to say, there is one and only one point of intersection between the two curves:

$$y=log\, sinh\, x-K$$

and

$$y=log\, sinh\frac{x}{n},$$

or again in other words, if $K>log n$, the value of B_o may be uniquely determined, what was to be proved.

If $$K<log\, n,$$

it is impossible to determine the value of B_o. which means that, to such an experimental curve the theoretical formulae are not to be applied, that is to say, that the reaction in this case did not proceed according to the assumptions previously made.

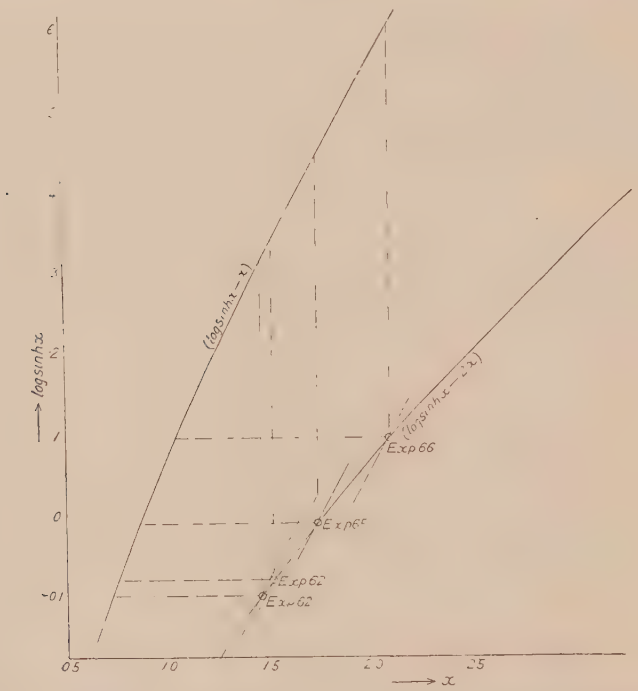
Hence it follows that, if at all the reaction proceeds as has been assumed, the value of K must be greater than that of $log\, n$ and consequently the value of B_o may be uniquely determined by the method hitherto considered.

Thus, if the value of B_0 is once determined, the value of A_0 may be calculated at once.

This general method may, as a matter of course, be applied to those cases where we can resort to the previous simplified methods.

By way of comparison, we will give a table of the values of B_0 obtained by the different methods together with those of t', t'', n', *log* and K.

Fig. 13.



No. of Experim.	t'	t''	n	$\log n$	K	B_0 obtained by the last method	B_0 obtained by the trial method	B_0 obtained by the approxim. method
50	20	10	2	0.301	0.733	0.164	—	0.164
55	30	15	2	0.301	1.496	0.230	—	0.229
58	20	10	2	0.301	0.997	0.230	—	0.228
60	18	9	2	0.301	0.774	0.196	—	0.199
62	11	5.5	2	0.301	0.432	0.150	0.152	—
65	18	9	2	0.301	0.448	0.0964	0.0964	—
66	22	11	2	0.301	0.506	0.0950	0.0943	—

The following constants may be calculated from the values k, A_o, B_o and M. The constant $m_o n_o/M$ may be calculated from $A_o B_o/kM$. This constant indicates the ratio of the number of the particles ready to react at the beginning of the reaction to the total number of the particles contained in the sample. Because, it may be written in the form

$$\frac{m_o n_o/m_o}{M/m_o} = \frac{n_o}{N}.$$

The constant $m_o A/M$ may be calculated from

$$\left(\frac{4B_o^2}{k} - k\right) \Big/ M.$$

One of the simultaneous equations previously considered on p. 41 is

$$\frac{dn}{dt} = Am,$$

where A represents the number of the spheres which are activated in a unit of time when the increase of weight of the sample is unity, that is, $m = 1$.

Now the constant may be written in the form

$$\frac{(m_o A)/m_o}{M/m_o} = \frac{A}{N}.$$

Hence the constant indicates what portion of the sample is activated each unit of time when $m = 1$.

By the way, A and m_o cannot be obtained separately, for we have nothing experimental about a single particle.

On the Temperature Change of the Constants

Now taking out those constants which have any physical meaning, that is, k, $m_o n_o/M$ and $m_o A/M$, their behaviour vis-à-vis the change of temperature will be considered.

The experiments carried out at one and the same temperature may give more or less different values for the same constant. But

with any one of these values for each temperature, it may yet be possible to know the general aspect of the relations of the constants to temperature.

A table of the constants and the curves obtained by plotting the values of the constants against temperature will be given below.

No. of Experim.	Temperature	k	$m_0 n_0/M$	$4\ m_0 A/M$
44	410°	0·075	0·32	0·0021
50	450	0·250	0·22	0·0051
55	480	0·352	0·23	0·0069
58	510	0·370	0·25	0·0056
60	551	0·284	0·39	0·0081
62	590	0·186	0·65	0·0097
65	625	0·175	0·91	0·0013

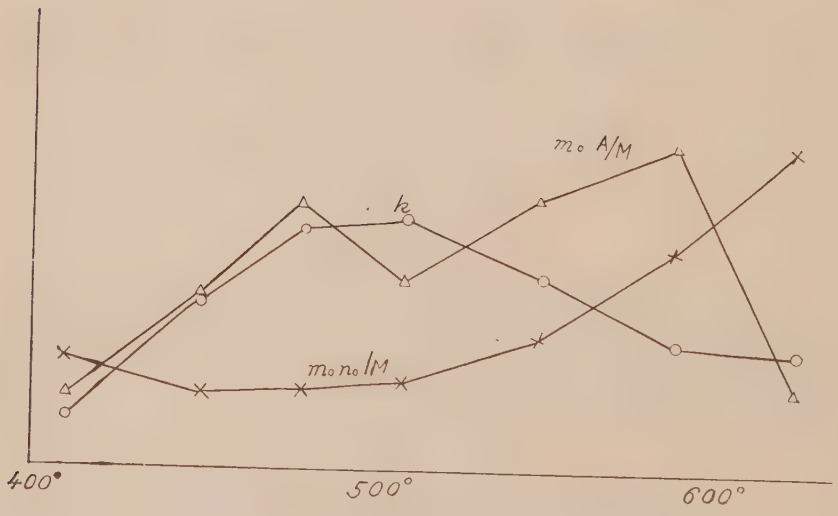


Fig. 14.

From the curves we see that

1. k has a maximum point at about 500°,
2. $m_0 n_0/M$ increases almost steadily,
3. $m_0 A/M$ has a maximum point at about 600°,

Now these relations of the constants to temperature may be explained by the following assumptions:

1. The rate of the absorption of oxygen (H) on the surface of a sphere and the rate of diffusion of substances in the solid (K) increase as temperature rises.

2. At lower temperatures, the sample is a more compact mass, consisting of smaller particles. At higher temperatures it becomes less compact, the particles increasing in size.

The temperature change of k.—The constant k (p. 36) is obviously a function of H and K, but it also depends upon the diameter of the sphere. Because, on page 35, we have seen that the inclination of the $dm/dt-m$ curve, defined by the equations

$$m = m_0 - \sum_{n=1}^{\infty} m_n e^{-\varkappa \alpha_n^2 t}$$

and

$$\frac{dm}{dt} = \sum_{n=1}^{\infty} m_n \varkappa \alpha_n^2 e^{-\varkappa \alpha_n^2 t},$$

when considered as a whole, changes inversely as the square of the radius of the sphere. Consequently, when we assume with approximation, that the diameter of the curve is a straight line, we must have a large or a small value of its inclination according as the diameter of the sphere is small or large.

The convergence of the curve to a straight line is the limiting case when the diameter tends to zero. With our concrete problem, however, we must not consider such an extreme case, but assume a certain very small but finite value of the diameter. Hence the dependence of k on the dimension of the sphere.

The constant k is obviously increased by the increase of H and K, while it is decreased by the increase of the dimension of the sphere.

If we now suppose that at lower temperatures the influence of H and K predominates while at higher temperatures the influence of the dimension of the sphere predominates in turn, the change of k with temperature may easily be understood.

The steady increase of $m_0 n_0/M$ follows directly from the assumption that the sample becomes less compact at higher temperatures. (With all this, the value of 0·91 at 625° may perhaps be too great.)

The temperature change of m_0A/M.—On page 39, it was assumed that the amount of the peroxide which acts as a loosening agent of the spheres, is a certain fraction of the amount of the peroxide normally formed on the active spheres. If we now assume that this fraction is the same for all temperatures, the amount of the peroxide which acts as a loosening agent must also be the same for all temperatures when $m=1$. This peroxide must cover the surface of the spheres in order to loosen them. But the volume of the spheres covered by a definite amount of the peroxide to a definite thickness of the covering film, is directly proportional to the radius of the sphere. Hence m_0A/M increases as temperature rises. On the other hand the peroxide formed on the surface will diffuse into the interior with greater velocity as temperature rises. Hence the diminution of m_0A/M with the elevation of temperature.

Thus the temperature variation of m_0A/M may now be explained by supposing that the increase of the constant due to the increase of radius of the sphere is more predominant at lower temperatures and the decrease of the constant due to the increase of velocity of diffusion is more predominant at higher temperatures.

Systematic experiments with air of varying water vapour content were not undertaken. Because in the present method of investigation, it was found necessary to perform experiments with one and the same sample in order to obtain any comparable result. It was desired, therefore, not to render possible any change more or less permanent in the sample by employing air rich in water vapour. But the fact is certain from the experiments performed with absolutely dry air, that if any water is necessary for the combination of barium oxide with oxygen, as is often stated in some books, it is only required to be present in the solid but not in the gaseons phase. Moreover, from a single experiment, it was found that the velocity of reaction was affected only half an hour after absolutely dry air was replaced by moist. This fact also confirms the above view.

Calculation of Constants

By means of the methods mentioned in the theoretical part, the constants occurring in the mathematical expressions,

$$\log m = \log A_0 + \log \sinh B_0 t - \frac{k}{2} \log e.t$$

and $$m = M(1 - e^{-[k-(\tau-\tau^0)]}),$$

will be determined in the following way. For this purpose, the data of the experiment 50 are taken as an example.

Determination of k.—In Fig. 15, the last portion of the experimental $m-t$ curve is shown on a larger scale and the values of dm/dt are determined by the tangents graphically drawn to the curve.

No.	m mg.	dm/dt
1	29·9	1·13
2	31·6	0·81
3	32·7	0·60
4	33·7	0·37
5	34·6	0·17
6	35·0	0·06

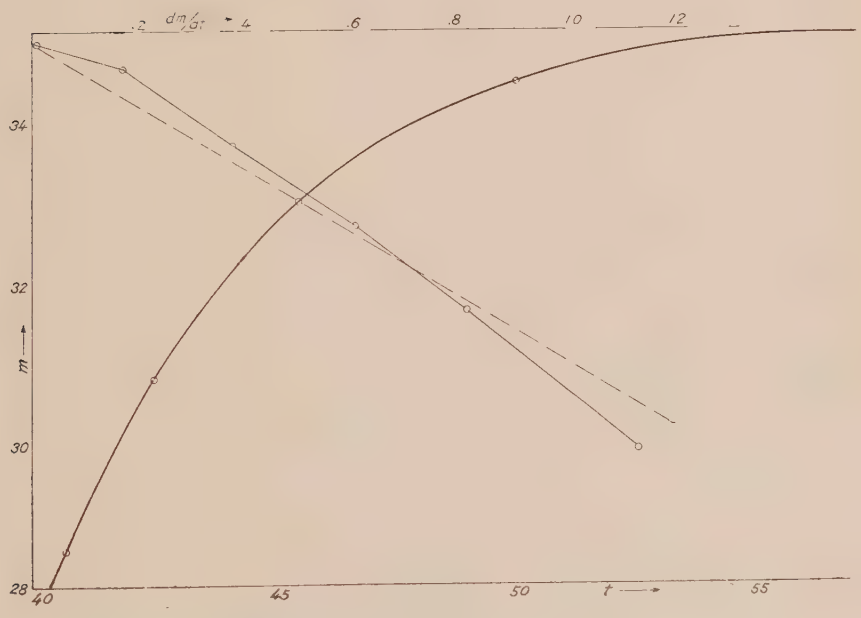


Fig. 15. Determination of k for Exp. 50.

The $dm/dt-m$ curve corresponding to this table is drawn in the same figure. A supposed straight line is then drawn with which the curve is to coincide, being denoted by a dotted line. The inclination of this straight line is the value of k, which is actually found to be

$$k=0{\cdot}25\,; \quad \text{hence} \quad \frac{k}{2}\log e=0{\cdot}0543.$$

Determination of A_0.—Fig. 16 shows the experimental $\log m-t$ curve. Producing its rectilinear portion, it is found

$$[\log m]_{t=0}=0{\cdot}77\,;$$

hence

$$\log A_0=0{\cdot}77-\log\frac{1}{2}=1{\cdot}07$$

Determination of B_0.—Subtracting

$$\frac{k}{2}\log e.\,40=2{\cdot}17$$

and

$$\log A_0=1{\cdot}07$$

from

$$(\log m)_{t=40}=1{\cdot}45,$$

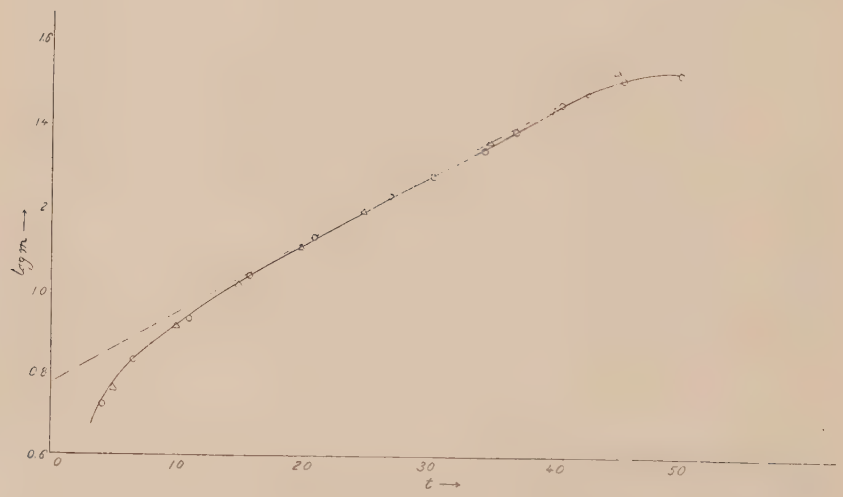


Fig. 16. $\log m-t$ curve for Exp. 50.

we have $\log \sinh (40\, B_0) = 2{\cdot}55.$

On the other hand, from the table of hyperbolic function, we have

$$\log \sinh 6{\cdot}56 = 2{\cdot}55\ ;$$

$$\therefore \quad B_0 = \frac{6{\cdot}56}{40} = 0{\cdot}164.$$

With these values of k, A_0 and B_0 we have the equation:

$$\log m = 1{\cdot}07 + \log \sinh 0{\cdot}164\, t - 0{\cdot}0543\, t,$$

from which follows the table:

t min.	$\log m$	m mg.
5	0·758	5·73
10	0·922	8·35
15	1·020	10·48
20	1·104	12·71
25	1·192	15·56
30	1·271	18·66
35	1·365	23·17
40	1·448	28·05
45	1·536	34·40

These calculated values of $\log m$ and m are shown in Figs. 16 and 17 with the points surrounded each by a small triangle.

Determination of μ, τ *and* τ_0.—μ is to be determined by the relation $\mu = \dfrac{kM}{\frac{k}{2} + B_0}$; where $M = 35{\cdot}1$ and k and B_0 are known constants.

By calculating, we have

$$\mu = 30{\cdot}4,$$

with which τ may be determined graphically, using the graph of the theoretical $m - t$ curve (Fig. 17):

$$\tau = 42.$$

Now $$\tau_o = \frac{\log \frac{M-\mu}{M}}{-k.\log e} = 8{\cdot}05$$

Hence the second equation becomes

$$m = 35{\cdot}1\ (1 - e^{-0{\cdot}25[t-34]}).$$

For different values of t, the corresponding values of m are calculated :

t min.	m mg.
44	32·2
49	34·3
54	34·9
59	35·1

In the following pages, numerical calculations are carried out with one experiment for each temperature, excepting the last two, in order to show to what degree the theory and the experiment agree.

For each experiment there are three figures. The first is for the determination of k. This figure shows the last part of the experimental $m-t$ curve. The values of dm/dt graphically obtained are plotted referring to an axis parallel to the $t-$axis. It must be noticed how the $dm/dt-m$ curve satisfies the requirement of the theory. The dotted straight line shown in the figure is an ideal one with which the experimental $dm/dt-m$ curve is to coincide, provided that the theory is correct and the observations are exact. The value of k is determined with this ideal line.

The second is for the determination of $[\log m]_{t=0}$. The figure shows the experimental $\log m-t$ curve. Notice its rectilinear portion.

The third shows the experimental $m-t$ curve.

In the latter two figures, the calculated values of $\log m$ and m are plotted by way of comparison. These calculated points are surrounded each by a small triangle while those obtained experimentally are surrounded each by a small circle.

The point of connection (μ, τ) of the two theoretical curves is closed in a small square.

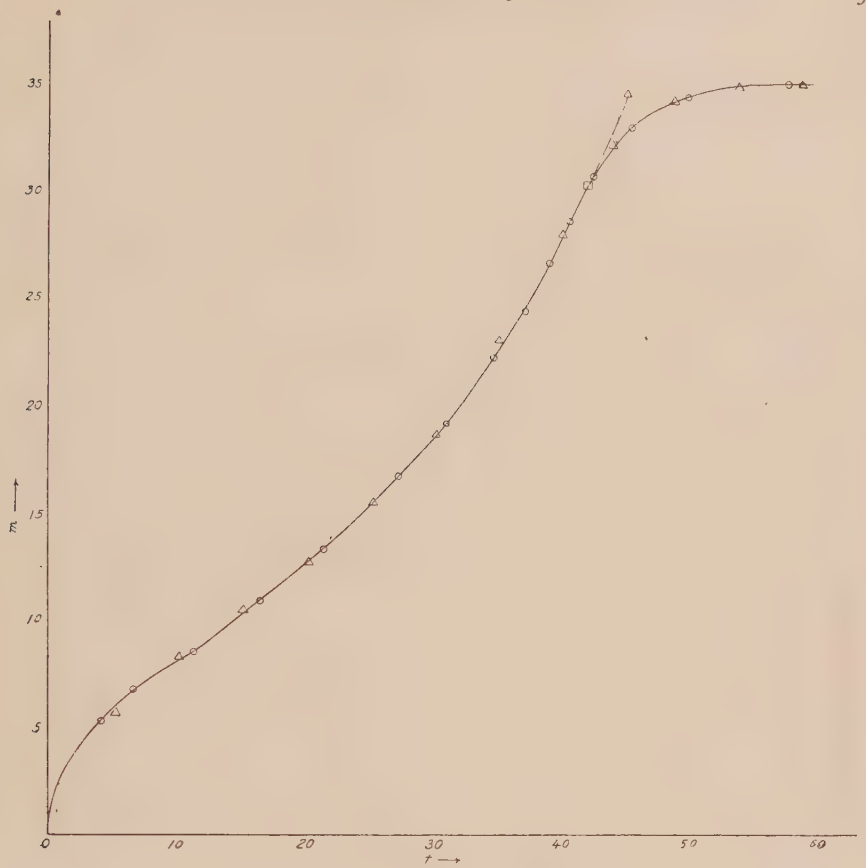


Fig. 17. $m-t$ curve for Exp. 50.

Exp. 44.

No.	m mg.	dm/dt
1	29·65	0·378
2	31·9	0·343
3	33·65	0·280
4	34·75	0·198
5	35·8	0·116

From the table we find $k=0·075$.

$$\therefore \quad \frac{k}{2} \log e = 0·0163;$$

with $[log\ m]_{t=0}=0{\cdot}92$ we get $log\ A_o=1{\cdot}22$;

and with $(log\ m)_{t=80}=1{\cdot}48$ we get $B_o=0{\cdot}0537$;

(I) $\therefore\ log\ m=1{\cdot}22+log\ sinh\ 0{\cdot}0537\ t-0{\cdot}0163\ t.$

Also with the values $\mu=30{\cdot}4$, $\tau_o=23$, $\tau=81{\cdot}3$ and $M=37$, we have

(II) $$m=37\ (1-e^{-0{\cdot}075\,[t-58{\cdot}3]}).$$

For a series of given values of t, the values of m are calculated with these two equations:

t min.	$log\ m$	m mg.	Equation used for the calculation.
10	0·809	6·44	(I)
20	1·006	10·14	,,
30	1·111	12·91	,,
40	1·193	15·60	,,
50	1·263	18·32	,,
60	1·332	21·48	,,
70	1·405	25·41	,,
80	1·480	30·20	,,
90	1·548	35·32	,,
100	1·620	41·69	,,
68·3		19·4	(II)
78·3		28·9	,,
88·3		33·2	,,
98·3		35·2	,,
108·3		36·0	,,
118·3		36·6	,,

Fig. 20 shows clearly how the two theoretical curves touch one another.

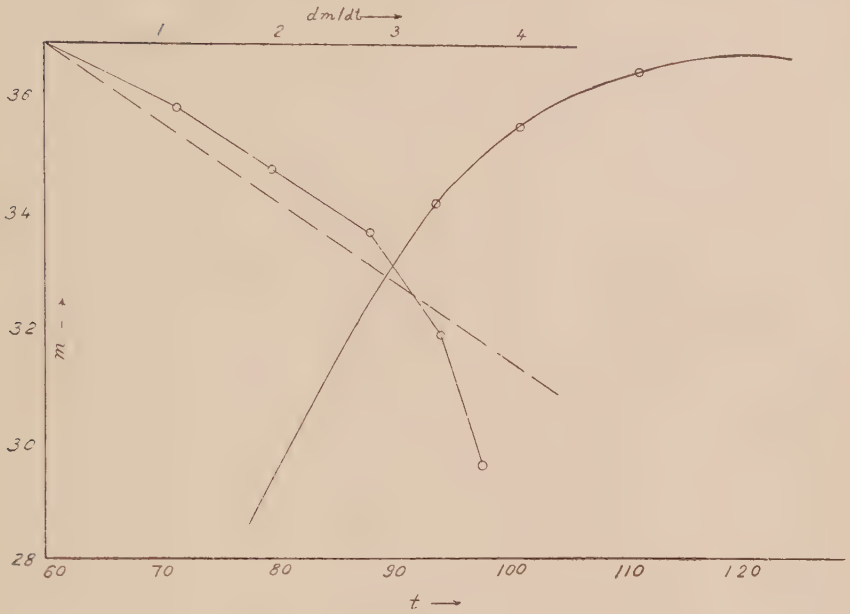


Fig. 18. Determination of k for Exp. 44.

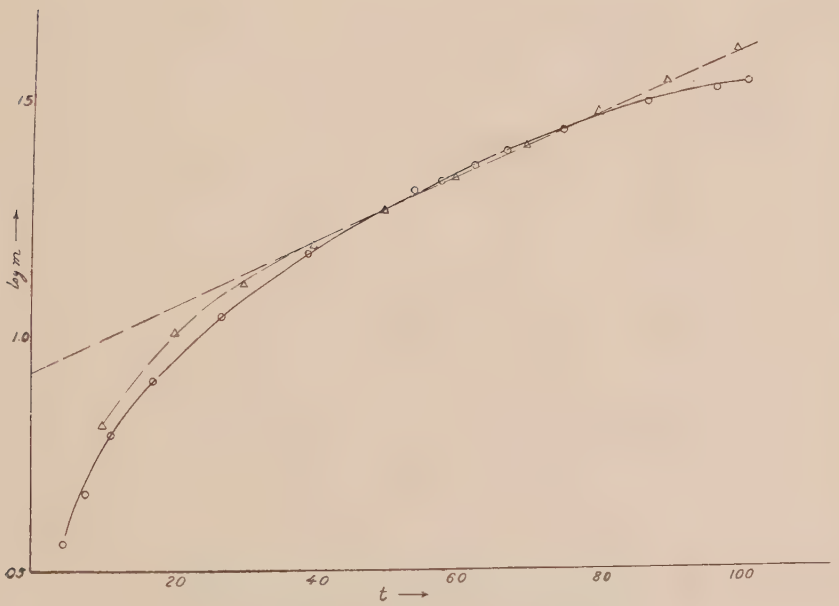


Fig. 19. $\log m - t$ curve for Exp. 44.

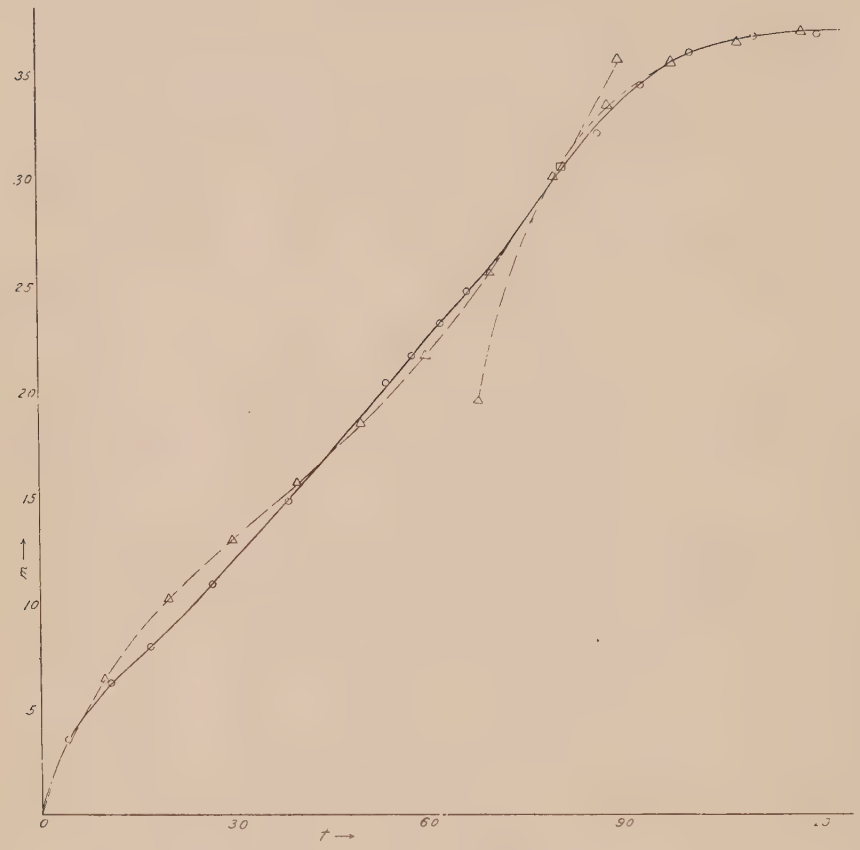


Fig. 20. $m-t$ curve for Exp. 44.

Exp. 55.

No.	m mg.	dm/dt
1	29·0	1·80
2	31·25	1·35
3	32·85	0·78
4	33·95	0·44
5	34·65	0·15

From the table we get $k=0{\cdot}352$;

$$\therefore \quad \frac{k}{2}\log e=0{\cdot}0764;$$

with $[\log m]_{t=0}=0{\cdot}79$ we get $\log A_0=1{\cdot}09$

and with $(\log m)_{t=30}=1{\cdot}49$ we get $B_0=0{\cdot}229$.

(I) $\therefore \quad \log m = 1{\cdot}09 + \log \sinh 0{\cdot}229\, t - 0{\cdot}0764\, t.$

Also with

$$\mu = 30{\cdot}4, \quad \tau_0 = 5{\cdot}71, \quad \tau = 29{\cdot}7 \text{ and } M = 35{\cdot}1$$

(II) we get $\quad m = 35{\cdot}1\ (1 - e^{-0{\cdot}352\,[t-24]}).$

For a series of given values of t, the values of m are calculated with the two equations:

t min.	$\log m$	m mg.	Equation used for the calculation.
5	0·858	7.21	(I)
10	1·016	10·38	,,
15	1·127	13·40	,,
20	1·249	17·74	,,
25	1·365	23·17	,,
30	1·490	30·90	,,
35	1·600	39·81	,,
31		32·1	(II)
34		34·1	,,
37		34·8	,,
40		35·0	,,
43		35·1	,,

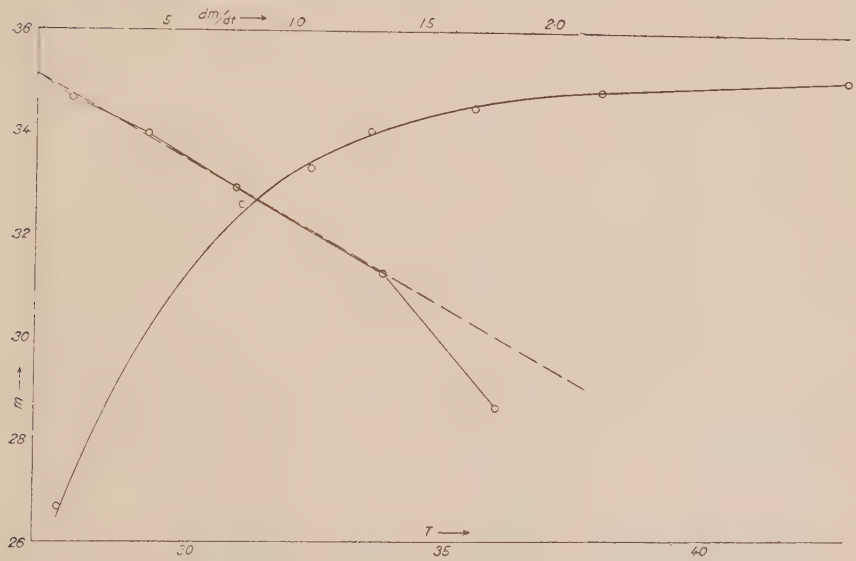


Fig. 21. Determination of k for Exp. 55.

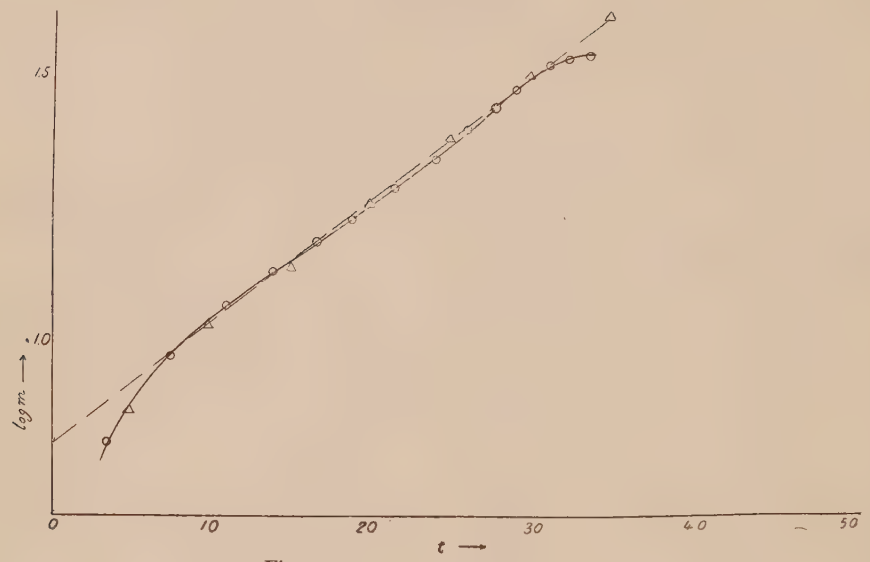


Fig. 22. *log m—t* curve for Exp. 55.

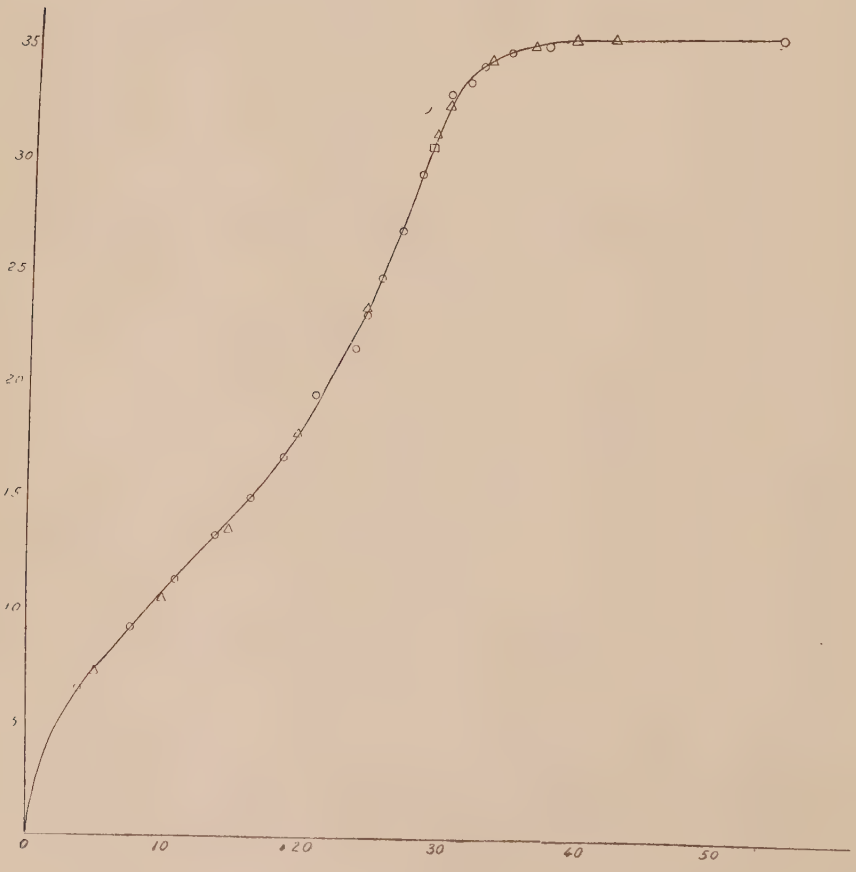


Fig. 23. *m—t* curve for Exp. 55.

Exp. 58.

No.	m mg.	dm/dt
1	30·15	1·57
2	31·15	1·15
3	32·0	0·84
4	32·8	0·59
5	33·4	0·38

From the table we get $k=0·37$ $\therefore$ $\frac{k}{2} \log e = 0·0802$;

with $[\log m]_{t=0}=0·84$ we get $\log A_0 = 1·14$

and with $(\log m)_{t=34}=1·47$ we get $B_0=0·228$.

(I) $\therefore$ $\log m = 1·14 + \log \sinh 0·228\, t - 0·0802\, t$.

Next with $\mu=30·8$, $\tau_0=6·12$. $\tau=34·6$ and $M=34·3$,

(II) we get $m=34·3\ (1-e^{-0·37\,[t-28·5]})$.

For a series of given values of t, the values of m are calculated with these two equations:

t min.	$\log m$	m mg.	Equation used for the calculation.
5	0·883	7·63	(I)
10	1·018	10·42	,,
15	1·112	12·94	,,
20	1·206	16·07	,,
25	1·298	19·86	,,
30	1·394	24·77	,,
35	1·500	31·62	,,
36.5		32·5	(II)
38.5		33·5	,,
40.5		34·0	,,
42.5		34·1	,,

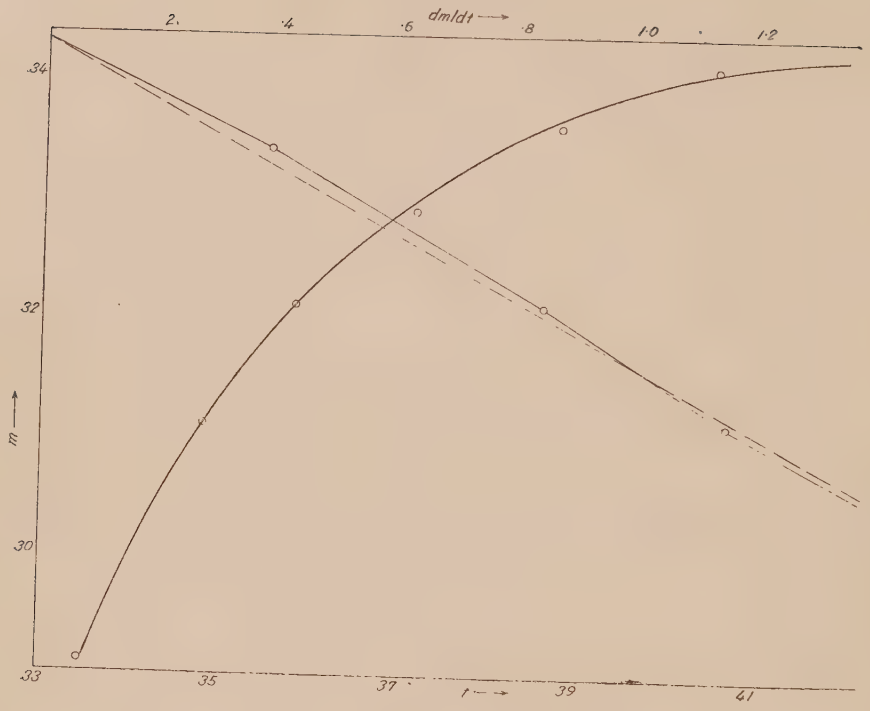


Fig. 24. Determination of k for Exp. 58.

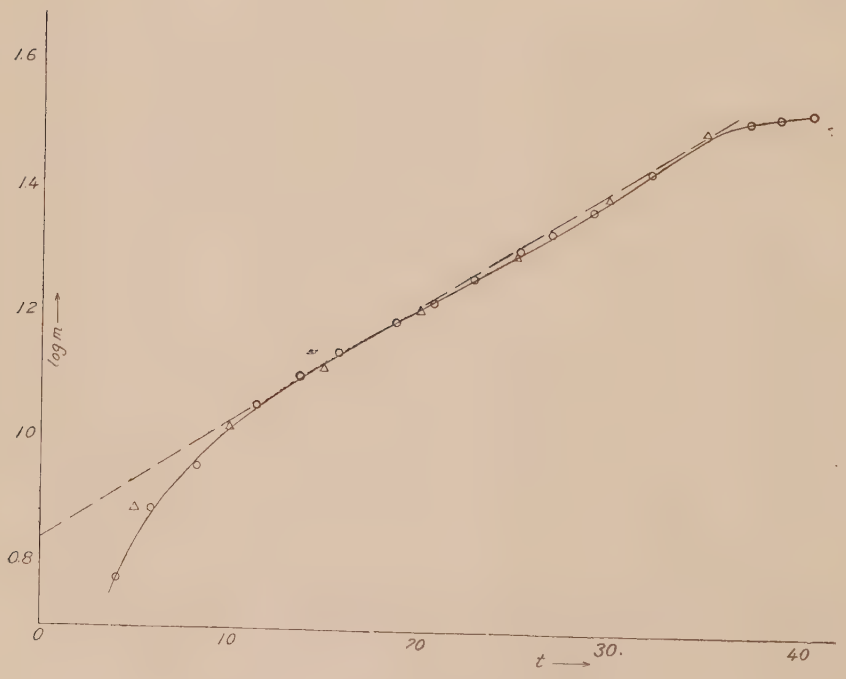


Fig. 25. $\log m - t$ curve for Exp. 58.

Fig. 26. $m-t$ curve for Exp. 58.

Exp. 60.

No.	m mg.	dm/dt
1	27·25	1·79
2	29·8	1·11
3	31·7	0·73
4	33·1	0·35
5	33·8	0·04

From the table we get $k=0{\cdot}284$,

$$\therefore \quad \frac{k}{2} \log e = 0{\cdot}0616\,;$$

with $[\log m]_{t=0}=0{\cdot}98$ we get $\log A_0 = 1{\cdot}28$

and with $(\log m)_{t=18} = 1{\cdot}46$ we get $B_0 = 0{\cdot}199$,

(I) $\therefore \quad \log m = 1{\cdot}28 + \log \sinh 0{\cdot}199\, t - 0{\cdot}0616\, t.$

Next with $\mu = 28{\cdot}3$, $\tau_0 = 6{\cdot}36$, $\tau = 19{\cdot}3$ and $M = 33{\cdot}9$,

(II) we get $m = 33{\cdot}9\ (1 - e^{-0{\cdot}284\,[t-13]})$.

For given values of t, the values of m are calculated with the two equations:

t min.	$\log m$	m mg.	Equation used for the calculation.
3	0·895	7·85	(I)
6	1·086	12·18	,,
9	1·194	15·62	,,
12	1·273	18·74	,,
15	1·341	21·93	,,
18	1·421	26·37	,,
20	1·473	29·72	,,
20		29·4	(II)
23		31·9	,,
26		33·1	,,
29		33·6	,,
31		33·8	,,
34		33·9	,,

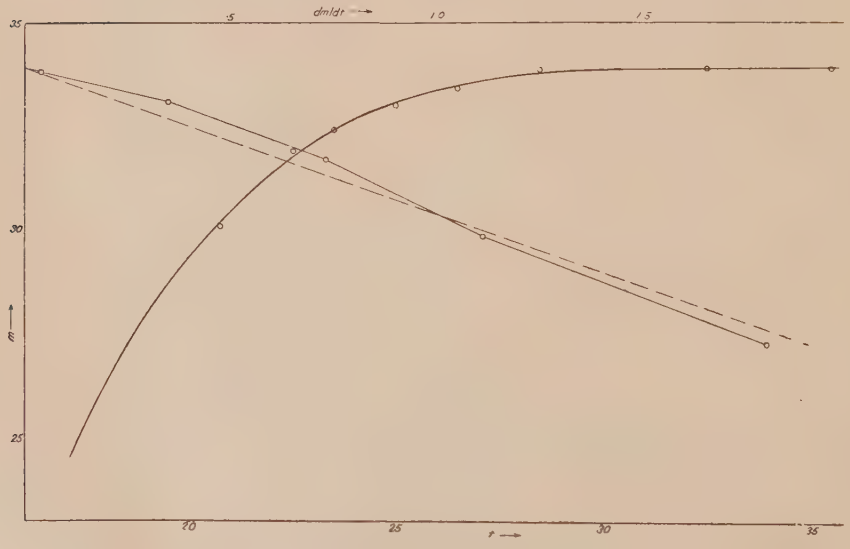


Fig. 27. Determination of k for Exp. 60.

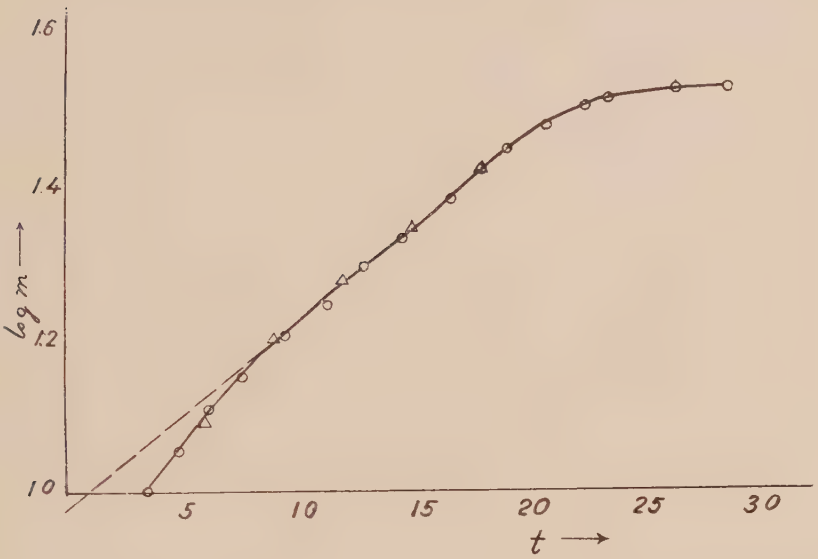


Fig. 28. *log m—t* curve for Exp. 60.

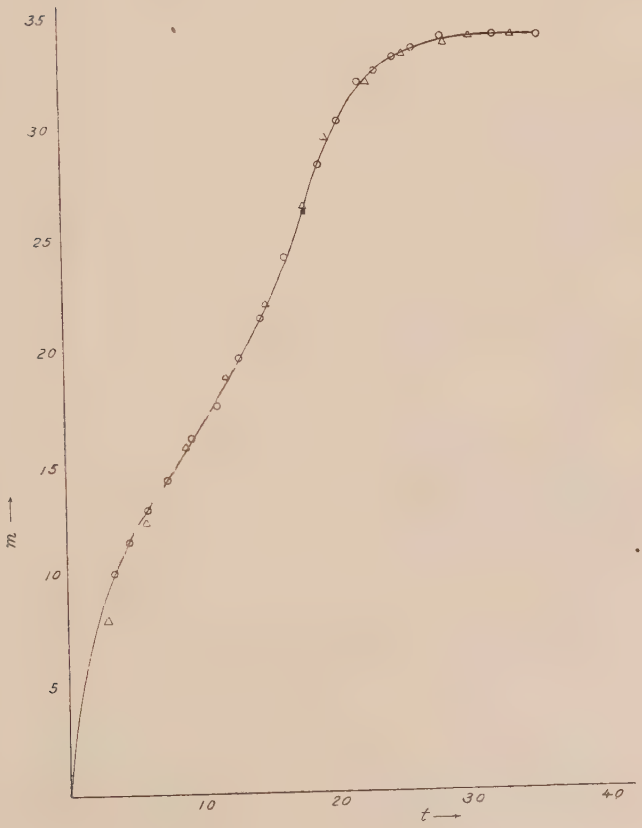


Fig. 29. *m—t* curve for Exp. 60.

Exp. 62.

No.	m mg.	dm/dt
1	22·45	1·780
2	25·25	1·085
3	27·75	0·708
4	29·30	0·476
5	31·10	0·165

From the table we get $k=0{\cdot}186$, $\therefore \quad \frac{k}{2}\log e=0{\cdot}0404$.

A_0 is determined by the trial method mentioned on page 50:

$$\log A_0=1{\cdot}4 \qquad \therefore \quad [\log m]_{t=0}=1{\cdot}1.$$

But $(\log m)_{t=10}=1{\cdot}33$; $\therefore \quad B_0=0{\cdot}152$.

(I) $\therefore \quad \log m=1{\cdot}4+\log \sinh 0{\cdot}152\,t-0{\cdot}0404\,t.$

Also μ cannot be calculated with the approximation formula used in the previous examples. As described on page 44, it must be determined graphically.

We have the following equation (cf. p. 45).

$$\frac{dm}{dt}=\frac{A_0}{2}\left[\left(-\frac{k}{2}+B_0\right)e^{(-\frac{k}{2}+B_0)t}+\left(\frac{k}{2}+B_0\right)e^{(-\frac{k}{2}-B_0)t}\right].$$

On substituting the numerical values of k, A_0 and B_0 in the above equation, we have

(II) $$\frac{dm}{dt}=12{\cdot}56\left[0{\cdot}059\,e^{0{\cdot}059\,t}+0{\cdot}245\,e^{-0{\cdot}245\,t}\right].$$

With equations (I) and (II), we may calculate the corresponding values of dm/dt and m, for given values of t:

t min.	m mg.	dm/dt
10	21·59	1·60
11	23·17	1·62
12	24·84	1·68

By plotting these pairs of values on the $dm/dt-m$ plane, we may obtain the point of intersection of this curve with the straight line corresponding to the second theoretical curve

$$\frac{dm}{dt}=k\ (M-m),$$

where $$M=61{\cdot}6.$$

From this point of intersection (in Fig. 30, it is enclosed by two small concentric circles), we find

$$\mu=22{\cdot}9, \quad \therefore \quad \tau=10{\cdot}8 \text{ and } \tau_0=7.$$

Hence we have

(III) $$m=31{\cdot}6\ (1-e^{-0{\cdot}186\,[t-3{\cdot}8]}).$$

Giving a series of numerical values to t, the values of m are calculated with equations (I) and (III).

t min.	$log\ m$	m mg.	Equation used for the calculation.
5	1·121	13·21	(I)
6	1·176	14·98	,,
7	1·227	16·88	,,
8	1·267	18·48	,,
9	1·301	20·02	,,
10	1·332	21·59	,,
11	1·366	23·17	,,
12	1·395	24·84	,,
20	1·604	40·18	,,
11 50		24·4	(III)
14 50		27·5	,,
17 50		29·3	,,
20 50		30·3	,,
23 50		30·8	,,
27 50		31·3	,,
31 50		31·5	,,
39 50		31·6	,,

The straight line to be used for the determination of A_o in the approximation method may be inversely obtained with the data:

$$t=20,\ (log\ m)_{t=20}=1\cdot604,\ [log\ m]_{t=0}=1\cdot1.$$

In the accompanying figure, (Fig. 31), it is shown with a chain line.

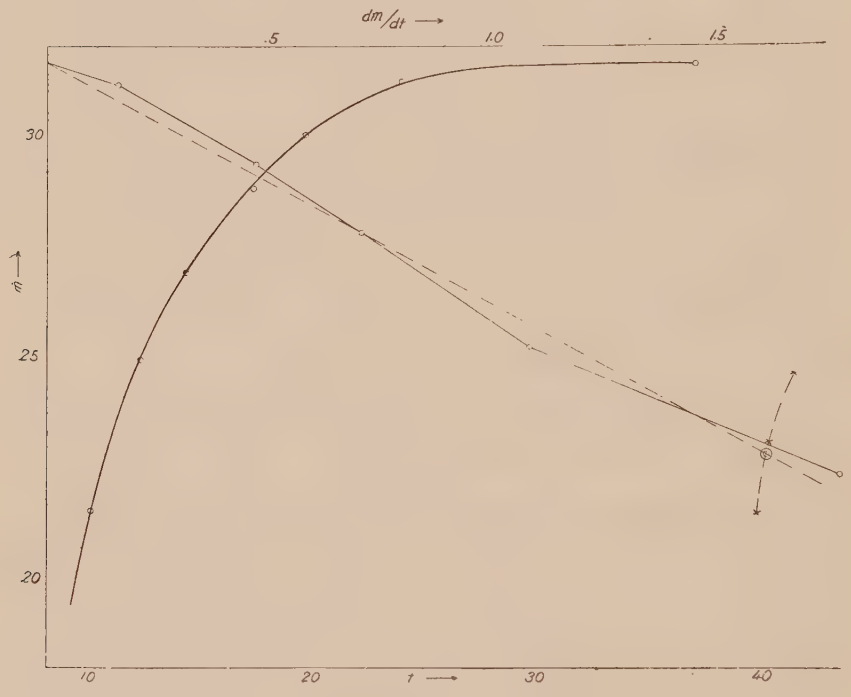


Fig. 30. Determination of for Exp. 62.

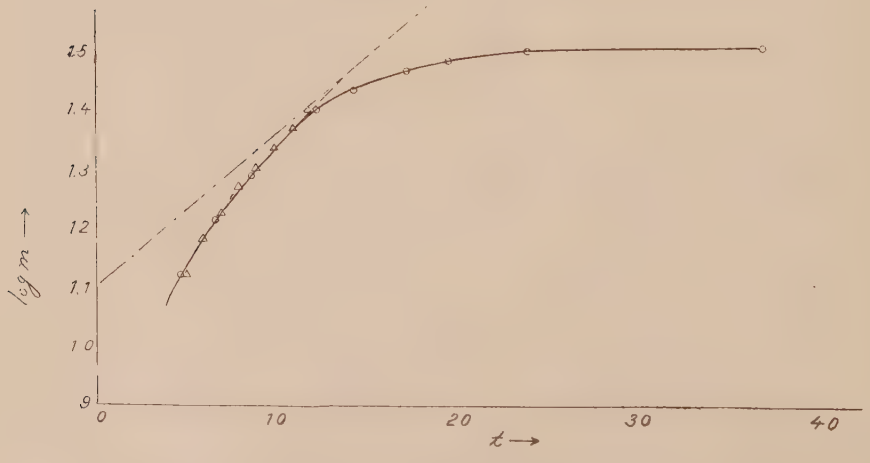


Fig. 31. $log\ m-t$ curve for Exp. 62.

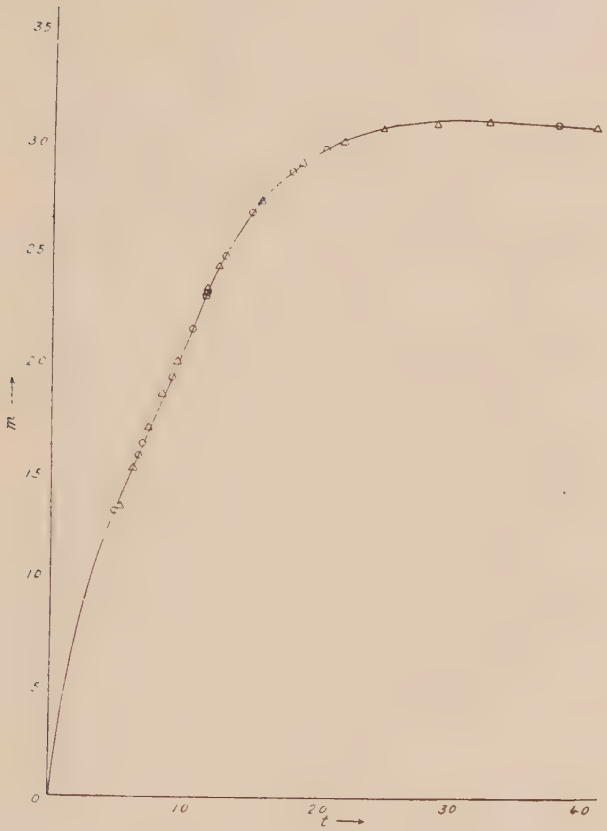


Fig. 32. $m-t$ curve for Exp. 62.

Exp. 65.

No.	m mg.	dm/dt
1	10·0	3·36
2	17·5	1·90
3	22·9	1·02
4	26·2	0·62
5	28·3	0·34
6	29·5	0·15

From the table we get

$$k=0\cdot175, \quad \therefore \quad \frac{k}{2}\log e=0\cdot038.$$

A_o is determined by the trial method:

$$\log A_o = 1{\cdot}7,$$

$$\therefore \quad [\log m]_{t=0} = 1{\cdot}4$$

and with $(\log m)_{t=18} = 1{\cdot}45$ we get $B_o = 0{\cdot}096$.

(I) $$\therefore \quad \log m = 1{\cdot}4 + \log \sinh 0{\cdot}096\, t - 0{\cdot}038\, t.$$

μ is determined in the same way as was done in the previous example; also we have

(II) $$\frac{dm}{dt} = 25\left[0{\cdot}0089\, e^{0{\cdot}0089\, t} + 0{\cdot}184\, e^{-0{\cdot}184 t}\right].$$

The corresponding values of m and dm/dt are calculated with equations (I) and (II), for given values of t:

t min.	m mg.	dm/dt
16	27·6	0.415
18	28·4	0·344
20	29·5	0·296

In Fig. 33, μ is found from a point surrounded by two small circles, *i.e.*

$$\mu = 27{\cdot}8$$

$$\therefore \quad \tau_o = 14{\cdot}5 \text{ and } \tau = 16{\cdot}2.$$

(III) $$\therefore \quad m = 30{\cdot}2\ (1 - e^{-0{\cdot}175[t - 1{\cdot}7]}).$$

Giving a series of numerical values to t, the values of m are calculated with equations (I) and (III):

t min.	$\log m$	m mg.	Equation used for the calculation.
3	1·066	11·64	(I)
5	1·208	16·14	,,
7	1·296	19·77	,,
9	1·350	22·39	,,
10	1·370	23·44	,,
12	1·404	25·35	,,

t min.	*log m*	*m* mg.	Equation used for the calculation.
14	1·422	26·42	(I)
16	1·442	27.67	,,
18	1·454	28·44	,,
20	1·470	29·51	,,
22	1·479	30·13	,,
40	1·552	35·65	,,
16·7		28·0	(III)
19·7		28·9	,,
22·7		29·5	,,
25·7		29·8	,,
28·7		30·0	,,
31·7		30·1	,,
34·7		30·2	,,

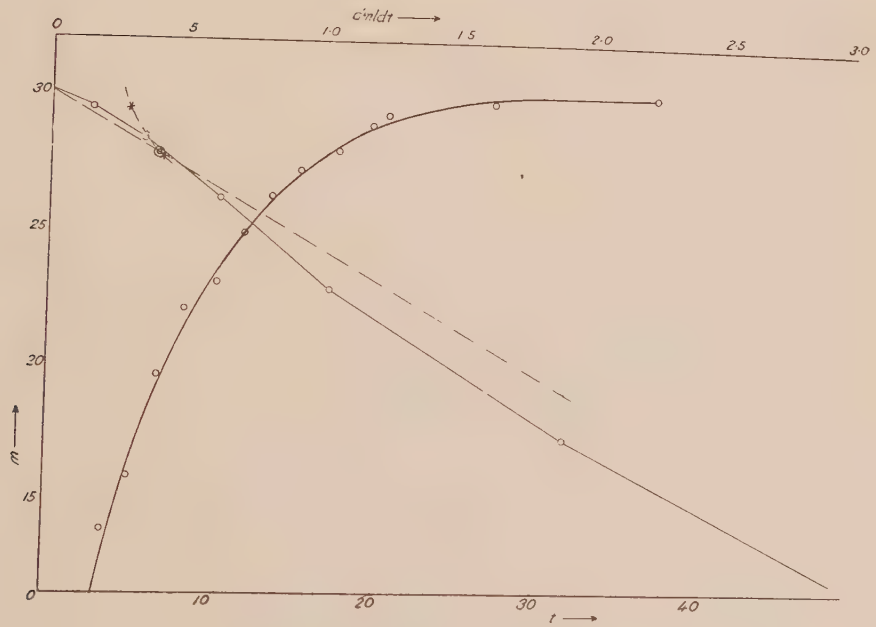


Fig. 33. Determination of k for Exp. 65.

In the reverse way, the straight line to be used for the determination of A_0 may be obtained with the data:

$$t=40,\ (log\ m)_{t=40}=1\cdot552,\ [log\ m]_{t=0}=1\cdot4.$$

It is denoted by the chain line in Fig. 34.

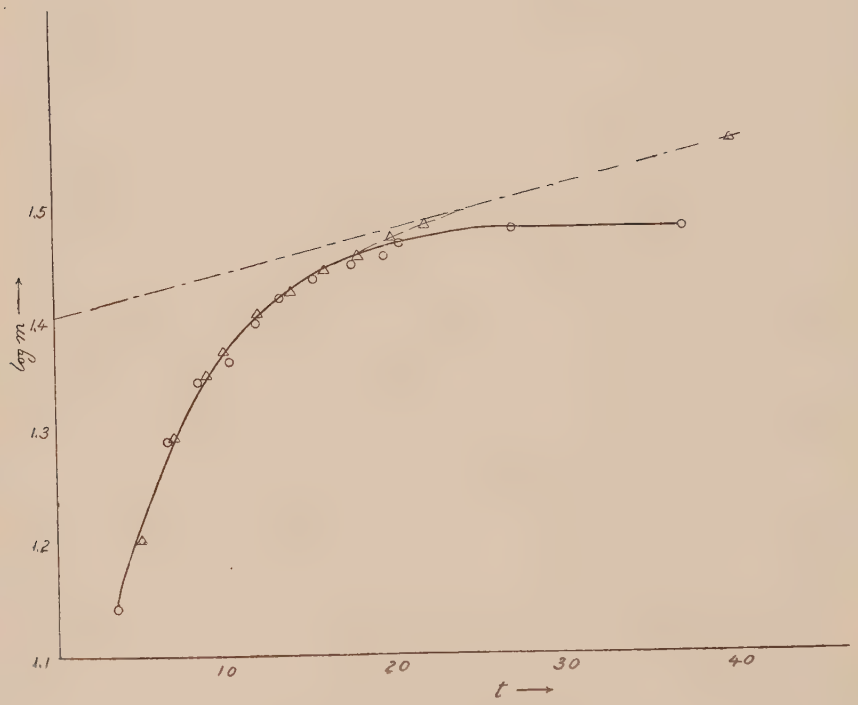


Fig. 34. $log\ m-t$ curve for Exp. 65.

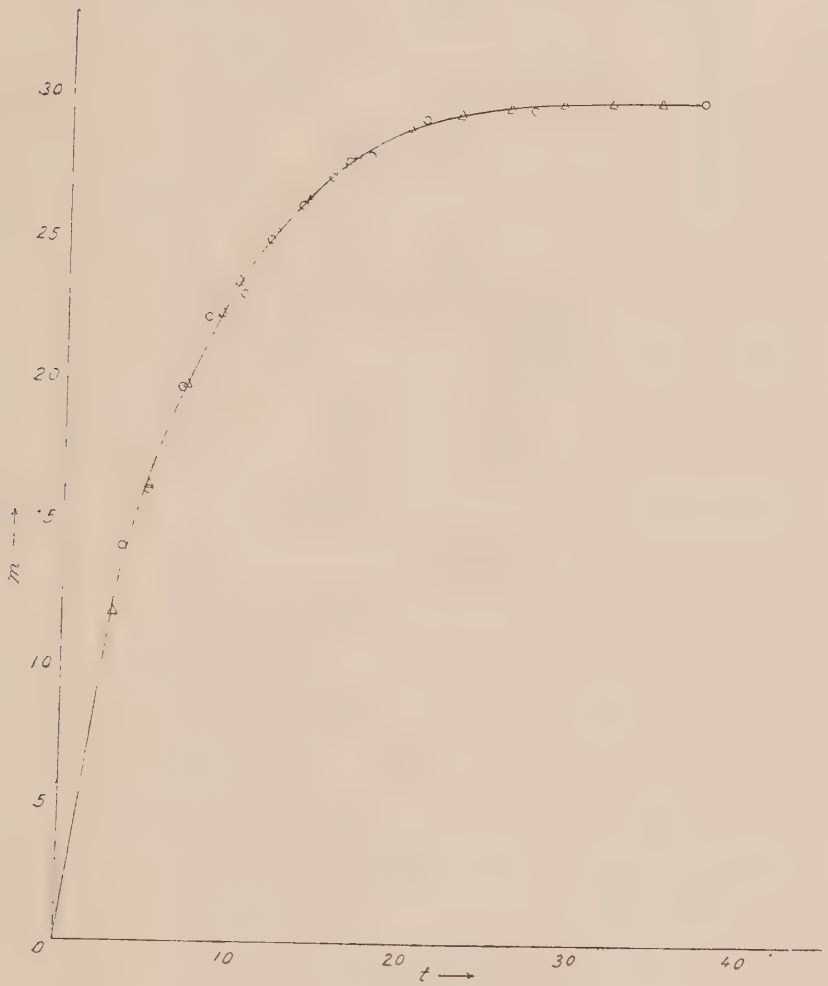


Fig. 35. $m-t$ curve for Exp. 65.

Exp. 66.

No.	m mg.	dm/dt
1	8·0	2·64
2	11·7	1·84
3	14·1	1·44
4	18·2	1·03
5	21·5	0·71
6	24·1	0·49
7	26·2	0·32
8	27·8	0.10

From the table we get

$$k=0{\cdot}165,$$

$$\therefore \quad \frac{k}{2}\log e=0{\cdot}0358.$$

As in the previous examples, it is found:

$$\log A_0=1{\cdot}61,$$

$$\therefore \quad [\log m]_{t=0}=1{\cdot}31,$$

and with $(\log m)_{t=22}=1{\cdot}417$ we get $B_0=0{\cdot}0943$.

(I) $$\therefore \quad \log m=1{\cdot}61+\log \sinh 0{\cdot}0943\, t-0{\cdot}0358\, t.$$

In order to determine μ, we use the equation

(II) $$\frac{dm}{dt}=20{\cdot}37\left(0{\cdot}0118\, e^{0{\cdot}0118\, t}+0{\cdot}177\, e^{-0{\cdot}177\, t}\right).$$

Calculating with (I) and (II), we get:

t min.	m mg.	dm/dt
15	22·8	0·555
18	24·3	0·459
21	25·7	0·404
24	26·5	0·377

Now μ may be determined graphically (cf. Fig.36):

$$\mu=26, \quad \therefore \quad \tau_0=15{\cdot}3 \text{ and } \tau=21{\cdot}8.$$

(III) $$\therefore \quad m=28{\cdot}3\left(1-e^{0{\cdot}165\,[t-6{\cdot}5]}\right).$$

With (I) and (III) we obtain by calculations :

t min.	*log m*	*m* mg.	Equation used for the calculation.
3	0·972	9·38	(I)
5	1·121	13·21	,,
7	1·207	16·11	,,
10	1·290	19·50	,,
12	1·323	21·04	,,
15	1·358	22·80	,,
18	1·385	24·27	,,
21	1·410	25·70	,,
24	1·430	26·92	,,
40	1·510	32·36	,,
21·5		25·9	(III)
24·5		26·8	,,
27·5		27·4	,,
31·5		27·9	,,
36·5		28·2	,,
41·5		28·3	,,

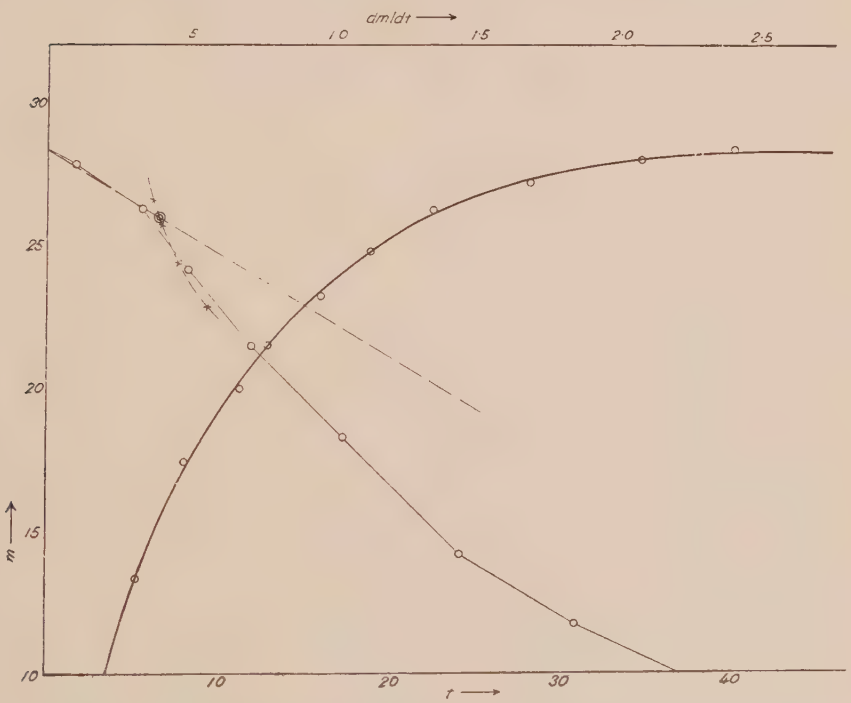


Fig. 36. Determination of k for Exp. 66.

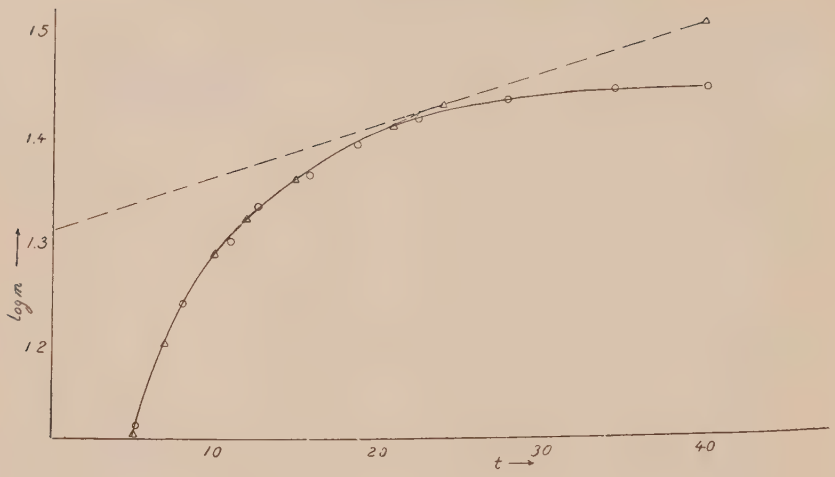


Fig. 37. *log m—t* curve for Exp. 66.

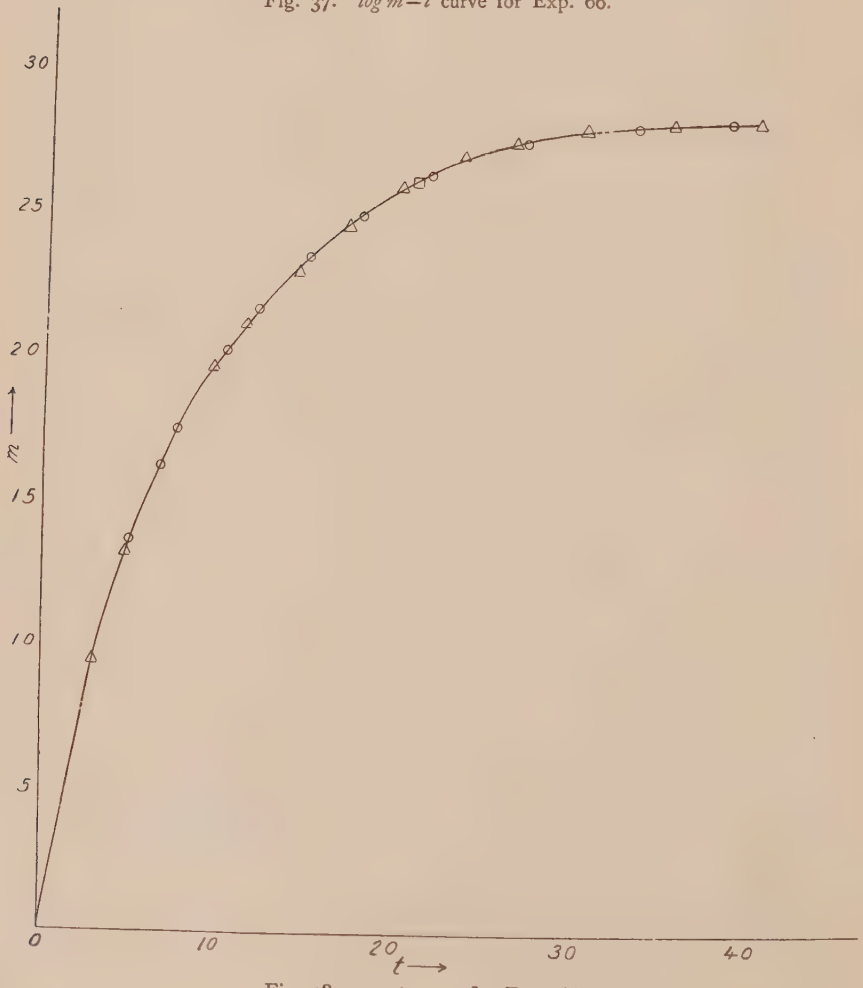


Fig. 38. *m—t* curve for Exp. 66.

Experimental Data

The following experimental data were obtained with one and the same sample. The pressure in the reaction chamber was always kept nearly at 720 mm. Hg. The air passed was dried either with concentrated sulphuric acid or with concentrated sulphuric acid and phosphorus pentoxide in series.

In the following tables, the figures in brackets indicate the number of the experiments. In the next is given the temperature at which the reaction took place. H_2SO_4 indicates that the air passed was dried with concentrated sulphuric acid. P_2O_5 indicates that it was dried with both conc. H_2SO_4 and P_2O_5. The column of t refers to the time of weighing and the column of m to the increase of weight.

The weight of the sample is not always the same at the beginning of the reaction, for the decomposition could not be carried to exactly the same degree in each experiment. The figures in brackets at the top of the column of m denote this deviation of initial weight from some arbitrary standard.

The amount of the peroxide in the sample at its final state is given in percentage by the figures in brackets at the end of the m column.

(41) 410°; H_2SO_4.

t hour	min.	m mg.	t hour	min.	m mg.
0	0	0(12·2)		47	22·3
	3·5	2·5	2	1	25·4
	9·5	3·7		15	27·7
	18·5	5·5		28	30·2
	30	8·0		46	33·3
	43·5	10·4	3	10	37·4
	56	12·7		26	38·3
1	9	15·6		30	38·3
	22	17·9			(83·0%)
	39	21·8			

(42) 410° ; H_2SO_4.

t hour min.	*m* mg.	*t* hour min.	*m* mg.
0 0	0(12·2)	47·5	25·8
3·5	1·5	55·5	30·4
6	3·6	1 0.5	32·6
11·5	5·8	8·5	35·3
16·5	7·9	19·5	37·2
28·5	14·5	33·5	37·8
37·5	20·0	47	37·8
44	23·6		(82·7%)

(43) 410° ; H_2SO_4.

t hour min.	*m* mg.	*t* hour min.	*m* mg.
0 0	0(13·5)	16·5	20·6
4·5	2·3	22	21·9
10·5	4·2	31	24·5
20	6·8	40	26·9
27	8·4	47	29·3
33·5	10·4	59	32·5
43	12·8	2 5	33·7
57	16·2	12·5	34·8
1 8·5	19·3	21	35·6
12	19·8		(81.9%)

(44) 410° ; H_2SO_4.

t hour min.	*m* mg.	*t* hour min.	*m* mg.
0 0	0(12.5)	1 2·5	23·0
4	3·6	6·5	24·6
6·5	4·6	15	27·6
11	6·2	26·5	31·9
17	8·0	33·5	34·2
27	10·9	41	35·5
39	14·8	51	36·5
50	18·4	2 6	36·5
54	20·3		(81·9%)
58	21·5		

(45) 410° ; H_2SO_4.

t hour	min.	*m* mg.	*t* hour	min.	*m* mg.
0	0	0(12·8)		14·5	27·3
	4·5	3·0		19	29·2
	9·5	4·0		22·5	30·4
	24·5	8·9		30	32·8
	29	10·4		27·5	34·5
	36	12·3		46	35·5
	40	13·8		55	35·9
	45·5	15·6	2	10	35·9
	55	19·3			(81·5%)
1	10·5	25·5			

(46) 410° ; H_2SO_4.

t hour	min.	*m* mg.	*t* hour	min.	*m* mg.
0	0	0(14·1)		33·5	23·9
	5·5	5·6		36·5	26·4
	8	6·8		45	31·9
	10·5	8·5		47	32·9
	15·5	11·5		51	34·1
	18	13·2		58·5	35·5
	22	16·0	1	11	36·0
	26·5	18·7		18	36·0
	30	21·4			(82·7%)

(47) 410° ; H_2SO_4.

t hour	min.	*m* mg.	*t* hour	min.	*m* mg.
0	0	0(14·8)		54	21·4
	5·5	4·0	1	1	23·6
	7·5	5·0		6	25·7
	11	6·0		12	28·7
	16·5	7·7		15	29·9
	20	9·0		21	32·4
	25	10·6		25	33·7
	32	12·8		29	34·5
	36	14·2		34	35·0
	42	16·3		42	35·3
	45·5	17·3			(82·7%)
	50	19·9			

(48) 450° ; H_2SO_4.

t hour	min.	*m* mg.	*t* hour	min.	*m* mg.
0	0	0(13·9)		43·5	26·8
	5	4·2		46·5	29·8
	10	6·5		50	32·4
	16	9·2		54	34·1
	20·5	11·2		58	34·9
	27	14·5	1	8	35·3
	33·5	19·0		35	35·3
	36·5	21·2			(81·9%)
	40·5	24·3			

(49) 450° ; H_2SO_4.

t hour	min.	*m* mg.	*t* hour	min.	*m* mg.
0	0	0(13·1)		37	22·5
	4·5	5·3		39·5	24·6
	7	6·5		43	27·9
	10·5	7·7		48	32·3
	12	8·5		51	34·4
	16·5	10·7		56	36·1
	22	13·0	1	2	36·4
	31	17·4			(82.2%)
	34	19·3			

(50) 450° ; H_2SO_4.

t hour	min.	*m* mg.	*t* hour	min.	*m* mg.
0	0	0(15·0)		37	24·5
	4	5·3		39	26·8
	6·5	6·7		40·5	28·7
	11	8·5		42·5	30·8
	16	10·9		48·5	33·0
	21	13·3		50	34·5
	27	16·7		58	35·1
	30·5	19·0	1	20	35·1
	34·5	22·3			(82·7%)

(51) 450° ; P_2O_5.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(14·7)	32		24·2
4	15	5·9	34	15	26·4
6	30	7·8	37	30	30·3
8	30	8·8	40	30	33·6
13		11·7	43		34·5
16		13·6	46	30	35·3
19		15·5	55		35·5
22		16·8	68		35·5
26	30	14·7			(82·8%)
30		22·5			

(52) 480° ; P_2O_5.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(14·9)	34	30	25·0
3	45	5·6	37		28·4
6	20	6·4	38		29·8
9	30	8·7	39	15	31·5
14		10·9	40	20	32·6
17	30	12·5	42		33·5
21		14·6	45		34·5
25		16·7	50		35·1
28	30	19·3			(82·6%)
32		22·1			

(53) 480° ; P_2O_5.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(15·4)	27	15	24·6
3	15	5·9	29		28·3
5	15	7·2	30	40	30·8
8		9·3	32	30	32·4
12		11·9	33	45	33·3
15		13·8	35	30	34·0
19	20	17·0	39		34·5
23		19·6	45		34·6
25	20	22·2			(82·6%)

(54) 480° ; P_2O_5.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(14·8)	28	30	25·9
3	30	6·0	29	40	27·7
5		6·9	31	30	30·6
6	30	8·1	33		32·7
9		9·5	35	15	33·5
14		12·3	36		34·3
17		14·0	37	30	35·0
20	30	17·0	42		35·5
23	30	19·5	50		35·7
25		21·6	60		35·9
26	30	23·4			(83·2%)

(55) 480° ; P_2O_5.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(15·4)	26		24·5
3	40	6·3	27	30	26·7
5		7·2	29		29·1
7	30	9·1	31		32·6
11		11·4	32	20	33·3
14		13·2	33	30	34·0
16	30	14·9	35	30	34·5
19		16·6	38		34·8
21	30	19·3	55		35·1
24		21·5			(83·1%)
25		23·6			

(56) 510° ; P_2O_5.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(15·9)	25		26·6
3	30	6·3	26	20	29·4
4	50	6·9	27	25	31·0
6	35	8·6	29		32·4
8	35	10·1	30	40	33·2
11	40	12·0	32		33·9
13	10	13·2	34	30	34·1
15	30	15·2	38		34·1
17	40	17·0	44		34·1
20	10	20·5			(82·6%)
22	15	22·0			

(57) 510° ; P_2O_5.

t min.	sec.	m mg.	t min.	sec.	m mg.
0	0	0(15·8)	26	30	22·8
3	20	6·0	28	50	26·2
5	30	7·6	30	20	28·9
8	30	10·0	32	30	32·0
11	30	11·8	34		33·1
14	30	13·8	35	10	33·8
17		15·3	36	15	34·1
19	30	17·0	38		34·4
21	40	18·3	48		34·5
23	50	20·3			(82·9%)

(58) 510° ; H_2SO_4.

t min.	sec.	m mg.	t min.	sec.	m mg.
0	0	0(16·2)	26	50	21·6
4		6·0	29		23·5
5	50	7·7	32	10	27·0
8	10	9·2	33	30	29·1
11	25	11·3	34	50	31·1
13	40	12·6	35	50	32·1
15	40	13·8	37	10	32·9
18	40	15·4	38	45	33·6
20	40	16·6	40	30	34·1
22	45	18·2			(82·9%)
25	10	20·1			

(59) 551° ; H_2SO_4.

t min.	sec.	m mg.	t min.	sec.	m mg.
0	0	0(16·2)	23	10	26·4
5	50	11·1	24	40	28·8
7	50	12·8	27	45	31·4
10		14·4	30	20	32·5
12		15·9	31	30	33·0
15		17·8	35	20	33·5
16	50	19·1	50		33·8
19		21·0			(82·6%)
20	45	23·1			

(60) 551° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(15·4)	19		28·1
3	20	10·0	20	45	30·1
4	45	11·3	22	30	31·9
6		12·7	23	30	32·4
7	30	14·1	25		33·0
9	20	15·9	26	30	33·4
11	15	17·4	28	30	33·9
13		19·5	32	30	33·9
14	40	21·3	35	30	33·9
16	35	24·0			(82·0%)
18		25·8			

(61) 551° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(16·2)	15	50	27·9
3	20	10·0	17		29·6
5	40	12·9	18		30·8
7	20	15·1	19	15	31·7
9		16·7	20	30	32·5
11		19·7	21	30	32·9
12	10	21·3	25		33·2
13	55	24·2	45		33·5
14	45	25·9			(82·4%)

(62) 590° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(16·6)	14	15	26·9
4	40	13·1	17	15	28·8
6	40	16·2	19	40	30·0
8	40	19·3	24		31·2
10		21·5	37		31·6
11		23·3			(81·0%)
12	15	24·9			

(63) 590° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(16·2)	14	45	26·9
3		10·5	16	20	28·3
4	45	12·7	17	45	29·6
6	20	15·6	21		30·7
8		19·9	23	5	31·1
9	30	21·9	29		31·7
11	10	22·8	33		31·7
12	50	25·3			(80·8%)

(64) 590° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(16·6)	14	30	22·6
3	15	9·3	15	30	23·5
5	10	11·7	17	45	26·2
6	30	13·0	19	10	27·1
7	20	14·3	21	30	28·5
9		16·0	25	30	29·7
10	20	18·6	27	30	30·3
13		20·9			(80·0%)

(65) 625° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(16·9)	15	15	27·2
3	30	14·0	17	30	28·0
5		16·0	19	30	28·9
6	45	19·7	20	30	29·3
8	20	22·1	27		29·8
10	15	23·1	37		30·2
11	50	24·9			(80·2%)
13	30	26·2			

(66) 625° ; H_2SO_4.

t min.	sec.	*m* mg.	*t* min.	sec.	*m* mg.
0	0	0(18·4)	18	40	24·7
5	10	13·4	22	20	26·2
8		17·4	28		27·3
11		20·0	34	30	28·0
12	40	21·5	40		28·3
15	40	23·2			(79·8%)

Summary

1. A new balance was devised which can be used completely from outside the balance case. It is, therefore, suitable for weighing a body at any temperature, under any pressure and in an atmosphere of any gas not reacting with the metals of the balance.

2. Two new types of gas washer were devised.

3. The velocity of the reaction between barium oxide and oxygen was found to be of very peculiar nature.

4. This peculiarity may, however, be explained by the assumptions that the oxide sample consisted of a great number of very small spherical particles of equal size and that these particles began to react one after the other according to a certain law.

5. With these assumptions, the mathematical expressions were deduced, and the calculated values were found to agree satisfactorily with those obtained by observation.

6. The temperature change of some constants occurring in the mathematical formulæ was discussed.

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